

- 1.4 Examine the statistics of fire. Is there any logical reason why the US death rate is among the highest and why Russia's increased so markedly after the fall of the Soviet Union?
- 1.5 The Oakland Hills fire in 1991 was a significant loss. Is the repetition of such fires due to earthquakes or the interface between the urban and wildlife domains? What is being done to mitigate or prevent these fires?
- 1.6 How does science enter into any of the codes and standards that you are familiar with?

## 2

## Thermochemistry

### 2.1 Introduction

Thermochemistry is the study of chemical reactions within the context of thermodynamics. Thermodynamics is the science of equilibrium states of matter which follow the conservation of mass and energy. Applications of the second law of thermodynamics can establish criteria for equilibrium and determine the possible changes of state. In general, changes of state take place over time, and states can vary over matter as spatial gradients. These gradients of states do not constitute equilibrium in the thermodynamic sense, yet it is justifiable to regard relationships between the thermodynamic properties to still apply at each point in a gradient field. This concept is regarded as local equilibrium. Thus the properties of temperature and pressure apply as well as their state relationships governed by thermodynamics. However, with regard to chemical properties, in application to fire and combustion, it is not usually practical to impose chemical equilibrium principles. Chemical equilibrium would impose a fixed distribution of mass among the species involved in the reaction. Because of the gradients in a real chemically reacting system, this equilibrium state is not reached. Hence, in practical applications, we will hypothesize the mass distribution of the reacting species or use measured data to prescribe it. The resultant states may not be consistent with chemical equilibrium, but all other aspects of thermodynamics will still apply. Therefore, we shall not include any further discussion of chemical equilibrium here, and the interested student is referred to any of the many excellent texts in thermodynamics that address this subject.

Where applications to industrial combustion systems involve a relatively limited set of fuels, fire seeks anything that can burn. With the exception of industrial incineration, the fuels for fire are nearly boundless. Let us first consider fire as combustion in the gas phase, excluding surface oxidation in the following. For liquids, we must first require evaporation to the gas phase and for solids we must have a similar phase transition. In the former, pure evaporation is the change of phase of the substance without changing its composition. Evaporation follows local thermodynamics equilibrium between the gas

and liquid phases. Heat is required to change the phase. Likewise, heat is required in the latter case for a solid, but now thermal decomposition is required. Except for a rare instance, of a subliming fuel, the fuel is not likely to retain much of its original composition. This thermal decomposition process is called pyrolysis, and the decomposed species can vary widely in kind and in number.

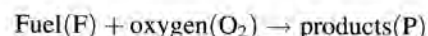
Fuels encountered in fire can be natural or manmade, the latter producing the most complications. For example, plastics constitute a multitude of synthetic polymers. A polymer is a large molecule composed of a bonded chain of a repeated chemical structure (monomer). For example, the polymers polyethylene and polymethyl-methylmethacrylate (PMMA) are composed of the monomers  $C_2H_4$  and  $C_5H_8O_2$  respectively. The  $C_2H_4$ , standing alone, is ethylene, a gas at normal room temperatures. The properties of these two substances are markedly different, as contrasted by their phase change temperatures:

	Ethylene	Polyethylene
Melt temperature( $^{\circ}C$ )	-169.1	$\sim 130$
Vaporization temperature( $^{\circ}C$ )	-103.7	$\sim 400$

For ethylene, the phase transition temperatures are precise, while for polyethylene these are very approximate. Indeed, we may have pyrolysis occurring for the polymer, and the phase changes will not then be so well defined. Moreover, commercial polymers will contain additives for various purposes which will affect the phase change process. For some polymers, a melting transition may not occur, and instead the transition is more complex. For example, wood and paper pyrolyze to a char, tars and gases. Char is generally composed of a porous matrix of carbon, but hydrogen and other elements can be attached. Tars are high molecular weight compounds that retain a liquid structure under normal temperatures. The remaining products of the pyrolysis of wood are gases consisting of a mixture of hydrocarbons, some of which might condense to form an aerosol indicative of the 'white smoke' seen when wood is heated. The principal ingredient of wood is cellulose, a natural polymer whose monomer is  $C_6H_{10}O_5$ . Wood and other charring materials present a very complex path to a gaseous fuel. Also wood and other materials can absorb water from the atmosphere. This moisture can then change both the physical and chemical properties of the solid fuel. Thus, the pyrolysis process is not unique for materials, and their description for application to fire must be generally empirical or very specific.

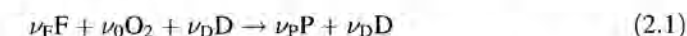
## 2.2 Chemical Reactions

Combustion reactions in fire involve oxygen for the most part represented as



The oxygen will mainly be derived from air. The fuel will usually consist of mostly carbon (C), hydrogen (H) and oxygen (O) atoms in a general molecular structure,  $F: C_xH_yO_z$ . Fuels could also contain nitrogen (N), e.g. polyurethane, or chlorine (Cl), e.g. polyvinylchloride  $(C_2H_3Cl)_n$ .

We use F as a representative molecular structure of the fuel in terms of its atoms and P, a similar description for the product. Of course, we can have more than one product, but symbolically we only need to represent one here. The chemical reaction can then be described by the chemical equation as



where the  $\nu$ 's are the stoichiometric coefficients. The stoichiometric coefficients are determined to conserve atoms between the left side of the equation, composing the reactants, and the right side, the products. In general,  $\nu_P P$  represents a sum over  $\nu_{P,i} P_i$  for each product species,  $i$ . Fuel or oxygen could be left over and included in the products, as well as an inert diluent (D) such as nitrogen in air, which is carried without change from the reactants to the products.

A complete chemical reaction is one in which the products are in their most stable state. Such a reaction is rare, but, in general, departure from it is small for combustion systems. For example, for the fuel  $C_xH_yO_z$ , the complete products of combustion are  $CO_2$  and  $H_2O$ . Departures from completeness can lead to additional incomplete products such as carbon monoxide (CO), hydrogen ( $H_2$ ) and soot (mostly C). For fuels containing N or Cl, incomplete products of combustion are more likely in fire, yielding hydrogen cyanide (HCN) and hydrogen chloride (HCl) gases instead of the corresponding stable products:  $N_2$  and  $Cl_2$ . In fire, we must rely on measurements to determine the incompleteness of the reaction. Where we might ignore these incomplete effects for thermal considerations, we cannot ignore their effects on toxicity and corrosivity of the combustion products.

A complete chemical reaction in which no fuel and no oxygen is left is called a stoichiometric reaction. This is used as a reference, and its corresponding stoichiometric oxygen to fuel mass ratio,  $r$ , can be determined from the chemical equation. A useful parameter to describe the state of the reactant mixture is the equivalence ratio,  $\phi$ , defined as

$$\phi = \left( \frac{\text{mass of available fuel}}{\text{mass of available oxygen}} \right) r \quad (2.2)$$

If  $\phi < 1$ , we have burned all of the available fuel and have leftover oxygen. This state is commonly called 'fuel-lean'. On the other hand, if  $\phi > 1$ , there is unburned gaseous fuel and all of the oxygen is consumed. This state is commonly called 'fuel-rich'. When we have a fire beginning within a room,  $\phi$  is less than 1, starting out as zero. As the fire grows, the fuel release can exceed the available oxygen supply. Room fires are termed ventilation-limited when  $\phi \geq 1$ .

The chemical equation described in Equation (2.1) can be thought of in terms of molecules for each species or in terms of mole ( $n$ ). One mole is defined as the mass ( $m$ ) of the species equal to its molecular weight ( $M$ ). Strictly, a mole (or mol) is a gram-mole (gmole) in which  $m$  is given in grams. We could similarly define a pound-mole (lb-mole), which would contain a different mass than a gmole. The molecular weight is defined as the sum of the atomic weights of each element in the compound. The atomic weights have been decided as a form of relative masses of the atoms with carbon (C) assigned the value of 12, corresponding to six protons and six neutrons.\* Thus, a mole is a relative

\* The average atomic weight for carbon is 12.011 because about 1 % of carbon found in nature is the isotope, carbon 13, having an extra neutron in the nucleus.

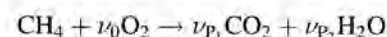
mass of the molecules of that species, and a mole and molecular mass are proportional. The constant of proportionality is Avogadro's number,  $N_0$ , which is  $6.022 \times 10^{23}$  molecules/mole. For example, the mass of a methane molecule is determined from  $\text{CH}_4$  using the atomic weights  $\text{C} = 12.011$  and  $\text{H} = 1.00794$ :

$$[(1)(12.011) + 4(1.00794)] \frac{\text{g}}{\text{mole}} \times \frac{1 \text{ mole}}{6.022 \times 10^{23} \text{ molecule}} = 2.66 \times 10^{-23} \frac{\text{g}}{\text{molecule}}$$

The chemical equation then represents a conservation of atoms, which ensures conservation of mass and an alternative view of the species as molecules or moles. The stoichiometric coefficients correspond to the number of molecules or moles of each species.

**Example 2.1** Ten grams of methane ( $\text{CH}_4$ ) are reacted with 120 g of  $\text{O}_2$ . Assume that the reaction is complete. Determine the mass of each species in the product mixture.

**Solution** The chemical equation is for the stoichiometric reaction:



where  $\nu_{\text{F}}$  was taken as 1. Thus,

$$\begin{array}{ll} \text{Conserving C atoms :} & \nu_{\text{P}_1} = 1 \\ \text{Conserving H atoms :} & 4 = 2\nu_{\text{P}_2} \quad \text{or} \quad \nu_{\text{P}_2} = 2 \\ \text{Conserving O atoms :} & 2\nu_0 = 2 + 2 \quad \text{or} \quad \nu_0 = 2 \end{array}$$

Hence,



as the stoichiometric reaction.

The reactants contain 10 g of  $\text{CH}_4$  and 120 g of  $\text{O}_2$ . The stoichiometric ratio is

$$r = \frac{m_{\text{O}_2}}{m_{\text{CH}_4}} \quad \text{for the stoichiometric reaction}$$

Since the stoichiometric reaction has 1 mole (or molecule) of  $\text{CH}_4$  and 2 moles of  $\text{O}_2$ , and the corresponding molecular weights are

$$M_{\text{CH}_4} = 12 + 4(1) = 16 \text{ g/mole}$$

as C has an approximate weight of 12 and H is 1, and

$$M_{\text{O}_2} = 2(16) = 32 \text{ g/mole}$$

we compute

$$r = \frac{(2 \text{ moles O}_2)(32 \text{ g/mole O}_2)}{(1 \text{ mole CH}_4)(16 \text{ g/mole CH}_4)} = 4 \text{ g O}_2/\text{g CH}_4$$

The equivalence ratio is then

$$\phi = \left( \frac{10 \text{ g CH}_4}{120 \text{ g O}_2} \right) (4) = \frac{1}{3} < 1$$

Therefore, we will have  $\text{O}_2$  left in the products. In the products, we have

$$\begin{aligned} m_{\text{O}_2} &= 120 \text{ g} - m_{\text{O}_2, \text{reacted}} \\ &= 120 \text{ g} - (10 \text{ g CH}_4) \left( \frac{4 \text{ g O}_2}{1 \text{ g CH}_4} \right) = 80 \text{ g O}_2 \end{aligned}$$

$$m_{\text{CO}_2} = (10 \text{ g CH}_4) \left( \frac{1 \text{ mole CO}_2}{1 \text{ mole CH}_4} \right) \left( \frac{44 \text{ g/mole CO}_2}{16 \text{ g/mole CH}_4} \right) = 27.5 \text{ g CO}_2$$

$$m_{\text{H}_2\text{O}} = (10 \text{ g CH}_4) \left( \frac{2 \text{ moles H}_2\text{O}}{1 \text{ mole CH}_4} \right) \left( \frac{18 \text{ g/mole H}_2\text{O}}{16 \text{ g/mole CH}_4} \right) = 22.5 \text{ g H}_2\text{O}$$

Note that mass is conserved as 130 g was in the reactant as well as the product mixture.

## 2.3 Gas Mixtures

Since we are mainly interested in combustion in the gas phase, we must be able to describe reacting gas mixtures. For a thermodynamic mixture, each species fills the complete volume ( $V$ ) of the mixture. For a mixture of  $N$  species, the mixture density ( $\rho$ ) is related to the individual species densities ( $\rho_i$ ) by

$$\rho = \sum_{i=1}^N \rho_i \quad (2.3)$$

Alternative ways to describe the distribution of species in the mixture are by mass fraction,

$$Y_i = \frac{\rho_i}{\rho} = \frac{m_i/V}{m/V} = \frac{m_i}{m} \quad (2.4)$$

and by mole fraction,

$$X_i = \frac{n_i}{n} \quad (2.5)$$

where  $n$  is the sum of the moles for each species in the mixture. By the definition of molecular weight, the molecular weight of a mixture is

$$M = \sum_{i=1}^N X_i M_i \quad (2.6)$$



It follows from Equations (2.4) and (2.6) that the mass and mole fractions are related as

$$Y_i = \frac{n_i M_i}{nM} = \frac{X_i M_i}{M} \quad (2.7)$$

**Example 2.2** Air has the approximate composition by mole fraction of 0.21 for oxygen and 0.79 for nitrogen. What is the molecular weight of air and what is its corresponding composition in mass fractions?

**Solution** By Equation (2.6),

$$\begin{aligned} M_a &= \left(0.21 \frac{\text{moles O}_2}{\text{mole air}}\right) (32 \text{ g/mole O}_2) \\ &\quad + \left(0.79 \frac{\text{moles N}_2}{\text{mole air}}\right) (28 \text{ g/mole N}_2) \\ M_a &= 28.84 \text{ g/mole air} \end{aligned}$$

By Equation (2.7),

$$Y_{\text{O}_2} = \frac{(0.21)(32)}{(28.84)} = 0.233$$

and

$$Y_{\text{N}_2} = 1 - Y_{\text{O}_2} = 0.767$$

The mixture we have just described, even with a chemical reaction, must obey thermodynamic relationships (except perhaps requirements of chemical equilibrium). Thermodynamic properties such as temperature ( $T$ ), pressure ( $p$ ) and density apply at each point in the system, even with gradients. Also, even at a point in the mixture we do not lose the macroscopic identity of a continuum so that the point retains the character of the mixture. However, at a point or infinitesimal mixture volume, each species has the same temperature according to thermal equilibrium.

It is convenient to represent a mixture of gases as that of perfect gases. A perfect gas is defined as following the relationship

$$p = \frac{nRT}{V} \quad (2.8)$$

where  $R$  is the universal gas constant,

$$8.314 \text{ J/mole K}$$

It can be shown that specific heats for a perfect gas only depend on temperature.

A consequence of mechanical equilibrium in a perfect gas mixture is that the pressures developed by each species sum to give the mixture pressure. This is known as Dalton's law, with the species pressure called the partial pressure,  $p_i$ :

$$p = \sum_{i=1}^N p_i \quad (2.9)$$

Since each species is a perfect gas for the same volume ( $V$ ), it follows that

$$\frac{p_i}{p} = \frac{n_i RT/V}{nRT/V} = \frac{n_i}{n} = X_i \quad (2.10)$$

This is an important relationship between the mole fraction and the ratio of partial and mixture pressures.

Sometimes mole fractions are called volume fractions. The volume that species  $i$  would occupy if allowed to equilibrate to the mixture pressure is

$$V_i = \frac{n_i RT}{p}$$

From Equation (2.8) we obtain

$$\frac{V_i}{V} = \frac{n_i}{n} = X_i$$

Hence, the name volume fraction applies.

## 2.4 Conservation Laws for Systems

A system is considered to be a collection of matter fixed in mass. It can exchange heat and work with its surroundings, but not mass. The conservation laws are expressed for systems and must be adjusted when the flow of matter is permitted. We will return to the flow case in Chapter 3, but for now we only consider systems.

The conservation of mass is trivial to express for a system since the mass ( $m$ ) is always fixed. For a change in the system from state 1 to state 2, this is expressed as

$$m_1 = m_2 \quad (2.11a)$$

or considering variations over time,

$$\frac{dm}{dt} = 0 \quad (2.11b)$$

Alternatively, the rate or time-integrated form applies to the system.

The conservation of momentum or Newton's second law of motion is expressed for a system as

$$\mathbf{F} = \frac{d(m\mathbf{v})}{dt} \quad (2.12)$$

where  $\mathbf{F}$  is the vector sum of forces acting on the system and  $\mathbf{v}$  is the velocity of the system. If  $\mathbf{v}$  varies over the domain of the system, we must integrate  $\rho\mathbf{v}$  over the system volume before we take the derivative with time. Implicit in the second law is that  $\mathbf{v}$  must be measured with respect to a 'fixed' reference frame, such as the Earth. This is called an inertial frame of reference. Although we will not use this law often in this book, it will be important in the study of fire plumes in Chapter 10.

Since our system contains reacting species we need a conservative law for each species. Consider the mass of species  $i$  ( $m_i$ ) as it reacts from its reactant state (1) to its product state (2). Then since the mass of  $i$  can change due to the chemical reaction with  $m_{i,r}$  being produced by the reaction

$$m_{i,2} = m_{i,1} + m_{i,r} \quad (2.13)$$

or as a rate

$$\frac{dm_i}{dt} = \dot{m}_{i,r} \quad (2.14)$$

The right-hand side of Equation (2.14) is the mass rate of production of species  $i$  due to the chemical reaction. This term represents a generation of mass. However, for the fuel or oxygen it can be a sink, having a negative sign. From Example 2.1,  $m_{O_2,2}$  is 80 g,  $m_{O_2,1}$  is 120 g and  $m_{O_2,r}$  is -40 g.

The conservation of energy or the first law of thermodynamics is expressed as the change in total energy of the system, which is equal to the net heat added to the system from the surroundings ( $Q$ ) minus the net work done by the system on the surroundings ( $W$ ). Energy ( $E$ ) is composed of kinetic energy due to macroscopic motion and internal energy ( $U$ ) due to microscopic effects. These quantities, given as capital letters, are extensive properties and depend on the mass of the system. Since each species in a mixture contributes to  $U$  we have for a system of volume ( $V$ ),

$$U = V \sum_{i=1}^N \rho_i u_i \quad (2.15)$$

where  $u_i$  is the intensive internal energy given as  $U_i/m_i$ . Since the mass of the system is fixed from Equations (2.4) and (2.5), it can be shown that

$$u = \sum_{i=1}^N Y_i u_i \quad (2.16)$$

or

$$\bar{u} = \sum_{i=1}^N X_i \bar{u}_i \quad (2.17)$$

where the designation  $(\bar{\phantom{x}})$  means per mole. Furthermore, since  $u$  and  $\bar{u}$  are intensive properties valid at a point, the relationships given in Equations (2.16) and (2.17) always hold at each point in a continuum. In all our applications, kinetic energy effects will be negligible, so an adequate expression for the first law is

$$U_2 - U_1 = Q - W \quad (2.18)$$

### 2.4.1 Constant pressure reaction

For systems with a chemical reaction, an important consideration is reactions that occur at constant pressure. This could represent a reaction in the atmosphere, such as a fire, in which the system is allowed to expand or contract according to the pressure of the surrounding atmosphere. Figure 2.1 illustrates this process for a system contained in a cylinder and also bounded by a frictionless and massless piston allowed to move so that the pressure is always constant on each side.

We consider the work term to be composed of that pertaining to forces associated with turning 'paddlewheel' shafts and shear stress ( $W_s$ ), and work associated with normal pressure forces ( $W_p$ ). For most applications in fire,  $W_s$  will not apply and therefore we will ignore it here. For the piston of face area,  $A$ , the work due to pressure ( $p$ ) on the surroundings, moving at a distance  $(x_2 - x_1)$ , is

$$W_p = pA(x_2 - x_1)$$

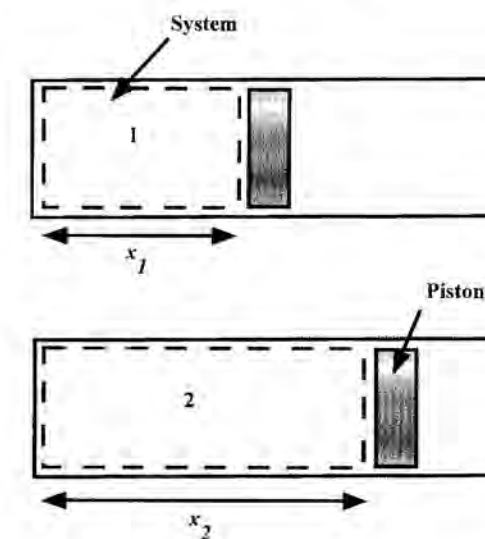


Figure 2.1 Constant pressure process

Since the volume of the system can be expressed by  $\Delta x$ ,

$$W_p = p(V_2 - V_1)$$

or

$$W_p = p_2 V_2 - p_1 V_1$$

since  $p_1 = p_2 = p$ . Then the first law (Equation (2.18)) becomes

$$U_2 - U_1 = Q - (p_2 V_2 - p_1 V_1)$$

The property enthalpy ( $H$ ), defined as

$$H = U + pV \quad (2.19)$$

is now introduced. Thus, for a constant pressure reacting system, without shaft or shear work, we have

$$H_2 - H_1 = Q \quad (2.20)$$

### 2.4.2 Heat of combustion

In a constant pressure combustion system in which state 1 represents the reactants and state 2 the products, we expect heat to be given to the surroundings. Therefore,  $Q$  is negative and so is the change in enthalpy according to Equation (2.20). A useful property of the reaction is the heat of combustion, which is related to this enthalpy change. We define the heat of combustion as the positive value of this enthalpy change per unit mass or mole of fuel reacted at 1 atm and in which the temperature of the system before and after the reaction is 25 °C. It is given as

$$\Delta h_c = - \frac{(H_2 - H_1)}{m_{F,r}} \quad (2.21a)$$

and

$$\Delta \tilde{h}_c = - \frac{(H_2 - H_1)}{n_{F,r}} \quad (2.21b)$$

with  $H_2$  and  $H_1$  evaluated at 1 atm, 25 °C. Often the heat of combustion is more restrictive in its definition, applying only to the stoichiometric (complete) reaction of the fuel. Sometimes the heat of combustion is given as a negative quantity which applies to Equation (2.21) without the minus sign before the parentheses. Since combustion gives rise to heat transfer, it is more rational to define it as positive. Also it should become apparent that the heat of combustion represents the contribution of energy from the sole process of rearranging the atoms into new molecules according to the chemical equation.

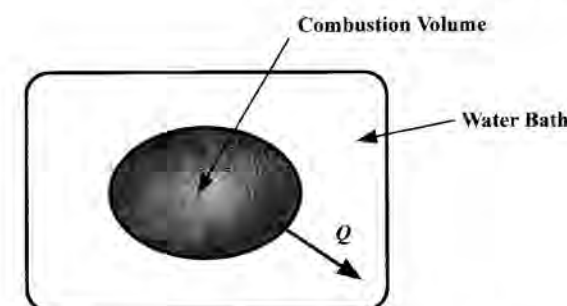


Figure 2.2 Idealized oxygen bomb calorimeter

In other words, there is no energy contribution due to a temperature change since it remains constant at 25 °C.

The heat of combustion of solids or liquids is usually measured in a device known as an oxygen bomb calorimeter. Such a device operates at a constant volume between states 1 and 2, and its heat loss is measured by means of the temperature rise to a surrounding water-bath. This is schematically shown in Figure 2.2. The combustion volume is charged with oxygen and a special fuel is added to ensure complete combustion of the fuel to be measured. Since the process is at constant volume ( $V$ ), we have

$$U_2 - U_1 = Q$$

from Equation (2.18). By the definition of enthalpy, we can write

$$H_2 - H_1 = Q + (p_2 - p_1)V$$

By analysis and by measurement, we can determine  $H_2 - H_1$  and express it in terms of values at 25 °C and 1 atm. Since  $Q$  is large for combustion reactions, these pressure corrections usually have a small effect on the accuracy of the heat of combustion determined in this way.

### 2.4.3 Adiabatic flame temperature

The adiabatic flame temperature is defined as the maximum possible temperature achieved by the reaction in a constant pressure process. It is usually based on the reactants initially at the standard state of 25 °C and 1 atm. From Equation (2.20), the adiabatic temperature ( $T_{ad}$ ) is determined from the state of the system at state 2 such that

$$H_2(T_{ad}) = H_1(25\text{ °C and } 1\text{ atm}) \quad (2.22)$$

We shall now see how we can express  $H_2$  in terms of the product mixture. It might be already intuitive, but we should realize that  $T_{ad}$  depends on the state of the reactants. In addition to the fuel, it depends on whether oxygen is left over, and if a diluent, such as nitrogen, must also be heated to state 2. Reactants that remain in the product state reduce



$T_{ad}$  since the energy associated with the combustion has been used to heat these species along with the new ones produced.

## 2.5 Heat of Formation

The molar heat of formation is the heat required to produce one mole of a substance from its elemental components at a fixed temperature and pressure. The fixed temperature and pressure is called the standard state and is taken at 25°C and 1 atm. The heat of formation is designated by the symbol  $\Delta h_{f,i}^\circ$  for the  $i$ th species and is given in energy units per unit mass or mole of species  $i$ . Usually, substances composed of a single element have  $\Delta h_{f,i}^\circ$  values at zero, but this is not always true since it depends on their state. For example, carbon as graphite is 0, but carbon as a diamond is 1.88 kJ/mole. Diamond has a different crystalline structure than the graphite, and thus it takes 1.88 kJ/mole to produce 1 mole of C (diamond) from 1 mole of C (graphite). This is a physical, not chemical, change of the molecular structure. Again, we are complying with the first law of thermodynamics in this process, but we do not know if or how the process can proceed.

An alternative, but equivalent, way to define the heat of formation of a species is to define it as the reference enthalpy at the standard state (25°C, 1 atm). Thus,

$$h_i(25^\circ\text{C}, 1 \text{ atm}) \equiv \Delta h_{f,i}^\circ \quad (2.23)$$

Strictly, this definition only applies to substances in equilibrium at the standard state.

For a perfect gas, and approximately for solids and liquids at small changes from 1 atm pressure, the enthalpy is only a function of temperature. It can be written in terms of specific heat at constant pressure,  $c_p$ , as

$$h_i(T) = \Delta h_{f,i}^\circ + \int_{25^\circ\text{C}}^T c_{p,i} dT \quad (2.24)$$

Strictly, this definition only applies to substances in equilibrium at the standard state. For the high temperatures achieved in combustion,  $c_p$  should always be regarded as a function of temperature. Some values are shown in Table 2.1. Values for the molar heats of formation for several substances are listed in Table 2.2. More extensive listings have been compiled and are available in reference books. The student should recognize that the values have been determined from measurements and from the application of Equation (2.20). Some examples should show the utility and interpretation of the heat of formation.

**Table 2.1** Specific heat at constant pressure,  $\bar{c}_{p,i}$  (J/K mole) (abstracted from Reference [1])

Temperature (K)	H <sub>2</sub> (g)	C(s)	CH <sub>4</sub> (g)	C <sub>2</sub> H <sub>4</sub> (g)	O <sub>2</sub> (g)	N <sub>2</sub> (g)	H <sub>2</sub> O(g)	CO <sub>2</sub> (g)	CO(g)
298	28.8	8.5	35.8	42.9	29.4	29.1	33.6	37.1	29.1
600	29.3	16.8	52.2	70.7	32.1	30.1	36.3	47.3	30.4
1000	30.2	21.6	71.8	110.0	34.9	32.7	41.3	54.3	33.2
1600	32.7	24.2	88.5	112.1	36.8	35.1	48.1	58.9	35.5
2500	35.8	25.9	98.8	123.1	38.9	36.6	53.9	61.5	36.8

(g) gaseous state, (s) graphite, solid state.

**Table 2.2** Heat of formation  $\Delta h_f^\circ$  in kJ/mole (at 25°C and 1 atm)<sup>a</sup> (abstracted from Reference [2])

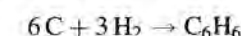
Substance	Formula	State	$\Delta h_f^\circ$ (kJ/mole)
Oxygen	O <sub>2</sub>	g	0
Nitrogen	N <sub>2</sub>	g	0
Graphite	C	s	0
Diamond	C	s	1.88
Carbon dioxide	CO <sub>2</sub>	g	-393.5
Carbon monoxide	CO	g	-110.5
Hydrogen	H <sub>2</sub>	g	0
Water	H <sub>2</sub> O	g	-241.8
Water	H <sub>2</sub> O	l	-285.9
Chlorine	Cl <sub>2</sub>	g	0
Hydrogen chloride	HCl	g	-92.3
Hydrogen cyanide	HCN	g	+135.1
Methane	CH <sub>4</sub>	g	-74.9
Propane	C <sub>3</sub> H <sub>8</sub>	g	-103.8
<i>n</i> -Butane	C <sub>4</sub> H <sub>10</sub>	g	-124.7
<i>n</i> -Heptane	C <sub>7</sub> H <sub>16</sub>	g	-187.8
Benzene	C <sub>6</sub> H <sub>6</sub>	g	+82.9
Formaldehyde	CH <sub>2</sub> O	g	-115.9
Methanol	CH <sub>3</sub> O	g	-201.2
Methanol	CH <sub>3</sub> O	l	-238.6
Ethanol	C <sub>2</sub> H <sub>5</sub> O	l	-277.7
Ethylene	C <sub>2</sub> H <sub>4</sub>	g	52.5

<sup>a</sup> Values for gaseous substances not in equilibrium at the standard state have been determined from the liquid and the heat of vaporization.

## 2.6 Application of Mass and Energy Conservation in Chemical Reactions

**Example 2.3** Consider the formation of benzene and carbon dioxide from their elemental substances. Find the heat required per unit mole at the standard state: 25°C, 1 atm.

**Solution** For benzene, formed from graphite and hydrogen gas,



is the chemical equation. By the application of Equation (2.20), we express the total enthalpies in molar form as

$$\tilde{H}_1 = (6 \text{ moles C})(\tilde{h}_\text{C}(25^\circ\text{C})) + (3 \text{ moles H}_2)(\tilde{h}_{\text{H}_2}(25^\circ\text{C}))$$

and

$$\tilde{H}_2 = (1 \text{ mole C}_6\text{H}_6)(\tilde{h}_{\text{C}_6\text{H}_6}(25^\circ\text{C}))$$

Since the enthalpies are the heats of formation by Equation (2.23), we find from Table 2.2 that

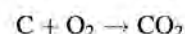
$$Q = \Delta \tilde{h}_f^\circ \text{ for benzene}$$

or

$$Q = +82.9 \text{ kJ/mole of benzene}$$

and heat is required.

In a similar fashion, obtaining carbon dioxide from graphite (carbon) and oxygen



gives  $-393.5 \text{ kJ/mole}$  for  $\text{CO}_2$  for  $Q$ , or heat is lost. This reaction can also be viewed as the combustion of carbon. Then by Equation (2.21b), this value taken as positive is exactly the heat of combustion of carbon; i.e.  $\Delta h_c = 393.5 \text{ kJ/mole carbon}$ .

**Example 2.4** Suppose we have the stoichiometric reaction for carbon leading to  $\text{CO}_2$ , but in the final state after the reaction the temperature increased from  $25$  to  $500^\circ\text{C}$ . Find the heat lost.

**Solution** Since state 1 is at  $25^\circ\text{C}$  for C and  $\text{O}_2$ , we obtain as before

$$\tilde{H}_1 = 0$$

However, at state 2, we write, from Equation (2.24),

$$\tilde{H}_2 = n_2 \tilde{h}_2 = (1 \text{ mole CO}_2) \left( \Delta \tilde{h}_f^\circ + \int_{25^\circ\text{C}}^{500^\circ\text{C}} c_p dT \right)$$

From Tables 2.1 and 2.2, we take a mean value of  $\tilde{c}_p = 47 \text{ J/mole K}$  and obtain

$$\tilde{H}_2 = (1 \text{ mole}) [-393.5 \text{ kJ/mole} + 47 \times 10^{-3} \text{ kJ/mole K}(475 \text{ K})]$$

or

$$\tilde{H}_2 = -371.2 \text{ kJ/mole}$$

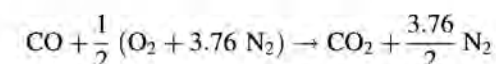
Therefore, the heat lost is  $371.2 \text{ kJ/mole}$ .

**Example 2.5** One mole of CO burns in air to form  $\text{CO}_2$  in a stoichiometric reaction. Determine the heat lost if the initial and final states are at  $25^\circ\text{C}$  and  $1 \text{ atm}$ .

**Solution** The stoichiometric reaction is



where all of the CO and all of the  $\text{O}_2$  in the air are consumed. It is convenient to represent air as composed of 1 mole  $\text{O}_2$  + 3.76 moles of  $\text{N}_2$ , which gives 4.76 moles of the mixture, air. These proportions are the same as  $X_{\text{O}_2} = 0.21$  and  $X_{\text{N}_2} = 0.79$ . The chemical equation is then



We designate state 1 as reactants and state 2 as the product mixture. By Equation (2.20),

$$Q = H_2 - H_1$$

Using molar enthalpies, we develop the total enthalpy of each mixture as

$$H = \sum_{i=1}^N n_i \tilde{h}_i$$

where  $\tilde{h}_i$  is found from Equation (2.24) and using Tables 2.1 and 2.2,

$$H_1 = (1 \text{ mole CO})(-110.5 \text{ kJ/mole}) + \frac{1}{2}(0) = -110.5 \text{ kJ}$$

$$H_2 = (1 \text{ mole CO}_2)(-393.5 \text{ kJ/mole}) + \left(\frac{3.76}{2}\right)(0) = -393.5 \text{ kJ}$$

$$Q = -393.5 - (-110.5) = -283.0 \text{ kJ}$$

From our definition of the heat of combustion, the result in Example 2.5 is unequivocally the heat of combustion of CO,  $\Delta \tilde{h}_c = 283 \text{ kJ/mole CO}$ , or  $\Delta \tilde{h}_c = 283/(12 + 16) = 10.1 \text{ kJ/g CO}$ . From Equations (2.21) and (2.24), we can generalize this result as

$$\Delta \tilde{h}_c = \left( \sum_{i=1}^N \nu_i \Delta \tilde{h}_{f,i}^\circ \right)_{\text{Reactants}} - \left( \sum_{i=1}^N \nu_i \Delta \tilde{h}_{f,i}^\circ \right)_{\text{Products}} \quad (2.25)$$

where the  $\nu_i$ 's are the molar stoichiometric coefficients with  $\nu_F$  is taken as one. Usually, tabulated values of  $\Delta h_c$  for fuels are given for a stoichiometric (complete) reaction. A distinction is sometimes given between  $\text{H}_2\text{O}$  being a liquid in the product state ('gross' value) or a gas ('net' value). The gross heat of combustion is higher than the net because some of the chemical energy has been used to vaporize the water. Indeed, the difference between the heats of formation of water in Table 2.2 for a liquid ( $-285.9 \text{ kJ/mole}$ ) and a gas ( $-241.8 \text{ kJ/mole}$ ) is the heat of vaporization at  $1 \text{ atm}$  and  $25^\circ\text{C}$ :

$$\Delta h_v = \frac{(285.9 - 241.8) \text{ kJ/mole}}{18 \text{ g/mole H}_2\text{O}} = 2.45 \text{ kJ/g H}_2\text{O}$$



**Example 2.6** Consider the same problem as in Example 2.5, but now with the products at a temperature of 625 °C.

**Solution** To avoid accounting for  $c_p$  variations with temperature, we assume constant average values. We select approximate average values from Table 2.1 as

$$c_{p,N_2} = 30 \text{ J/mole N}_2 \text{ K}$$

$$c_{p,CO_2} = 47 \text{ J/mole CO}_2 \text{ K}$$

Then for  $H_2$  we write

$$H_2 = \sum_{i=1}^2 \nu_i [\Delta h_{f,i} + c_{p,i}(T_2 - 25^\circ\text{C})]$$

where we sum over the products  $CO_2$  and  $N_2$ :

$$\begin{aligned} H_2 &= (1 \text{ mole } CO_2) \left[ -393.5 \text{ kJ/mole } CO_2 + 0.047 \text{ kJ/mole K}(600 \text{ K}) \right] \\ &\quad + \left( \frac{3.76}{2} \text{ moles } N_2 \right) \left[ 0 + 0.030 \text{ kJ/mole K}(600 \text{ K}) \right] \\ &= (-393.5) + \left[ (1)(0.047) + \left( \frac{3.76}{2} \right)(0.030) \right] (600) \\ &= (-393.5) + (0.10325)(600) \\ &= -331.55 \text{ kJ} \\ Q &= H_2 - H_1 = (-331.55) - (-110.5) = -221.05 \text{ kJ} \end{aligned}$$

For Example 2.6 we see that the heat lost due to the chemical reaction is composed of two parts: one comes from the heats of formation and the other from energy stored in the products mixture to raise its temperature. It can be inferred from these examples that we can write

$$(-Q) = \nu_F \Delta \tilde{h}_c + \sum_{i=1}^{N_{\text{Reactants}}} n_i \tilde{c}_{p,i} (T_1 - 25^\circ\text{C}) - \sum_{i=1}^{N_{\text{Products}}} n_i \tilde{c}_{p,i} (T_2 - 25^\circ\text{C}) \quad (2.26)$$

where  $\nu_F$  is the moles (or mass) of fuel reacted and  $n_i$  are the moles (or mass) of each species in the mixture before (1, reactants) and after (2, products) the reaction. If we

further consider specific heat of the mixture, since from Equations (2.17), (2.19), (2.24) and (2.25)

$$\begin{aligned} \tilde{c}_p &= \left( \frac{\partial \tilde{h}}{\partial T} \right)_p = \frac{\partial}{\partial T} \left( \sum X_i h_i \right) = \sum X_i \tilde{c}_{p,i} \\ &= \left( \frac{1}{n} \right) \sum n_i \tilde{c}_{p,i} \end{aligned} \quad (2.27)$$

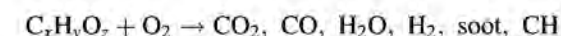
then

$$\begin{aligned} (-Q) &= \nu_F \Delta \tilde{h}_c + n_1 \tilde{c}_{p,1} (T_1 - 25^\circ\text{C}) \\ &\quad - n_2 \tilde{c}_{p,2} (T_2 - 25^\circ\text{C}) \end{aligned} \quad (2.28)$$

In other words, the heat lost in the chemical reaction is given by a chemical energy release plus a 'sensible' energy associated with the heat capacity and temperature change of the mixture states.

## 2.7 Combustion Products in Fire

Up to now we have only considered prescribed reactions. Given a reaction, the tools of thermodynamics can give us the heat of combustion and other information. In a combustion reaction we could impose conditions of chemical equilibrium, or ideally complete combustion. While these approximations can be useful, for actual fire processes we must rely on experimental data for the reaction. The interaction of turbulence and temperature variations can lead to incomplete products of combustion. For fuels involving  $C_xH_yO_z$  we might expect that

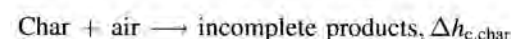
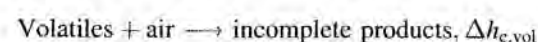


where soot is mostly carbon and by CH we mean the residual of hydrocarbons. Unless one can show a chemical similarity among the various burning conditions, the combustion products will be dependent on the experimental conditions.

Tewarson [3] has studied the burning characteristics of a wide range of materials. He has carried out experiments mainly for horizontal samples of 10 cm × 10 cm under controlled radiant heating and air supply conditions. Chemical measurements to determine the species in the exhaust gases have identified the principal products of combustion. Measurement of the mass loss of the sample during combustion will yield the mass of gas evolved from the burning sample. This gas may not entirely be fuel since it could contain evaporated water or inert fire retardants. It is convenient to express the products of combustion, including the chemical energy liberated, in terms of this mass loss. This is defined as a yield, i.e.

$$\text{yield of combustion product } i, y_i \equiv \frac{\text{mass of species } i}{\text{mass loss of sample}}$$

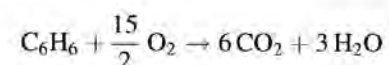
Values of yields for various fuels are listed in Table 2.3. We see that even burning a pure gaseous fuel as butane in air, the combustion is not complete with some carbon monoxide, soot and other hydrocarbons found in the products of combustion. Due to the incompleteness of combustion the 'actual' heat of combustion (42.6 kJ/g) is less than the 'ideal' value (45.4 kJ/g) for complete combustion to carbon dioxide and water. Note that although the heats of combustion can range from about 10 to 50 kJ/g, the values expressed in terms of oxygen consumed in the reaction ( $\Delta h_{O_2}$ ) are fairly constant at  $13.0 \pm 0.3$  kJ/g  $O_2$ . For charring materials such as wood, the difference between the actual and ideal heats of combustion are due to distinctions in the combustion of the volatiles and subsequent oxidation of the char, as well as due to incomplete combustion. For example,



$$\Delta h_{c,\text{wood}} = \Delta h_{c,\text{vol}} + \Delta h_{c,\text{char}}$$

where here the heats of combustion should all be considered expressed in terms of the mass of the original wood. For fuels that completely gasify to the same chemical state as in a phase change for a pure substance, the yield is equivalent to the stoichiometric coefficient. However, for a fuel such as wood, which only partially gasifies and the gaseous products are no longer the original wood chemical, we cannot equate yield to a stoichiometric coefficient. The use of 'yield' is both practical and necessary in characterizing such complex fuels.

Let us examine the measured benzene reaction given in Table 2.3. From the ideal complete stoichiometric reaction we have



The ideal heat of combustion is computed from Equation (2.25) using Table 2.2 as the net value ( $\text{H}_2\text{O}$  as a gas)

$$\begin{aligned} \Delta \bar{h}_c &= [(1)(+82.9)] - [(6)(-393.5) + (3)(-241.8)] \\ &= 3169.3 \text{ kJ/mole C}_6\text{H}_6 \end{aligned}$$

or

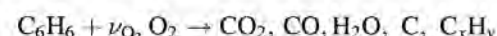
$$\Delta h_c = (3169.3)/(78 \text{ g/mole}) = 40.6 \text{ kJ/g}$$

This is higher than the value given in Table 2.3 (i.e., 40.2 kJ/g) since we used benzene from Table 2.2 as a gas and here it was burned as a liquid. The difference in energy went into vaporizing the liquid benzene and was approximately 0.4 kJ/g. (See Table 6.1)

Table 2.3 Products of combustion in fire with sufficient air (abstracted from Tewarson [31])

Substance	Formula	Heat of combustion $\Delta h_c$		Heat of combustion per mass of $O_2$ $\Delta h_{O_2}$	Actual yields (g products/g mass lost)			
		Ideal (kJ/g fuel burned)	Actual (kJ/g mass loss)		$CO_2$	CO	Soot	Other hydrocarbon
Methane (g)	$CH_4$	50.1	49.6	12.5	2.72	—	—	—
Propane (g)	$C_3H_8$	46.0	43.7	12.9	2.85	0.005	0.024	0.003
Butane (g)	$C_4H_{10}$	45.4	42.6	12.6	2.85	0.007	0.029	0.003
Methanol (l)	$CH_4O$	20.0	19.1	13.4	1.31	0.001	—	—
Ethanol (l)	$C_2H_6O$	27.7	25.6	13.2	1.77	0.001	0.008	0.001
n-Heptane (l)	$C_7H_{16}$	44.6	41.2	12.7	2.85	0.010	0.037	0.004
Benzene (g)	$C_6H_6$	40.2	27.6	13.0	2.33	0.067	0.181	0.018
Wood (red oak)	$CH_{1.7}O_{0.72}$	17.1	12.4	13.2	1.27	0.004	0.015	0.001
Nylon	$(C_6H_{11}NO)_n$	30.8	27.1	11.9	2.06	0.038	0.075	0.016
PMMA	$(C_5H_8O_2)_n$	25.2	24.2	13.1	2.12	0.010	0.022	0.001
Polyethylene, PE	$(C_2H_4)_n$	43.6	30.8	12.8	2.76	0.024	0.060	0.007
Polypropylene, PS	$(C_3H_6)_n$	43.4	38.6	12.7	2.79	0.024	0.059	0.006
Polystyrene, PS	$(C_8H_8)_n$	39.2	27.0	12.7	2.33	0.060	0.164	0.014

Let us continue further with this type of analysis, but now consider the actual reaction measured. We treat soot as pure carbon and represent the residual hydrocarbons as  $C_xH_y$ . Then the equation, without the proper coefficients, is



Since benzene is a pure substance and we continue to treat it as a gas, we can regard the yields in this case as stoichiometric coefficients. From the measured yields in Table 2.3 and the molecular weights

	$C_6H_6$	$O_2$	$CO_2$	$CO$	$C$	$C_xH_y$
$M_i$ (g/mole)	78	32	44	28	12	$12x + y$

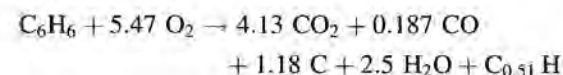
We calculate the stoichiometric coefficients,  $\nu_i$ :

$$\begin{aligned} CO_2 : \quad & 2.33 \text{ g } CO_2 / \text{g } C_6H_6 \left( \frac{78}{44} \right) = 4.13 \\ CO : \quad & (0.067) \left( \frac{78}{28} \right) = 0.187 \\ C : \quad & (0.181) \left( \frac{78}{12} \right) = 1.177 \\ \text{Total} \quad & 5.494 \approx 5.49 \end{aligned}$$

Since we must have six carbon atoms, we estimate  $x = 0.51$  and balance the H and O atoms:

$$\begin{aligned} H : \quad & 6 = 2\nu_{H_2O} + y \\ O : \quad & 2\nu_{O_2} = (2)(4.13) + (0.187) + \nu_{H_2O}(1) \end{aligned}$$

Selecting arbitrarily  $y = 1$ , we obtain



Since we do not know the composition of the hydrocarbons, we cannot deal correctly with the equivalent compound  $C_{0.51}H$ . This is likely to be a mixture of many hydrocarbons including  $H_2$ . However, for purposes of including its effect on the actual heat of combustion, we will regard it as  $\frac{1}{4} C_2H_4$ , ethylene, as an approximation. Then, as before, we compute the heat of combustion:

$$\begin{aligned} \Delta \tilde{h}_c &= [(1)(+82.9)] - [(4.13)(-393.5) + (0.187)(-110.5) \\ &\quad + (1.18)(0) + (2.5)(-241.8) + (0.25)(+52.5)] \\ \Delta \tilde{h}_c &= 2320.1 \text{ kJ/mole } C_6H_6 \end{aligned}$$

or

$$\Delta \tilde{h}_c = 29.7 \text{ kJ/g } C_6H_6$$

This is very close to the value given in Table 2.3 determined by measurements (i.e. 27.6 kJ/g).

One method of obtaining the chemical energy release in a fire is to measure the amount of oxygen used. Alternatively, some have considered basing this on the  $CO_2$  and  $CO$  produced. Both methods are based on the interesting fact that calculation of the heat of combustion based on the oxygen consumed, or alternatively the  $CO_2$  and  $CO$  produced, is nearly invariant over a wide range of materials. Huggett [4] demonstrated this for typical fire reactions, and Table 2.3 illustrates its typical variation. For the stoichiometric benzene reaction, it is listed in Table 2.3 as 13.0 kJ/g  $O_2$ . For the actual benzene reaction from our estimated result, we would obtain

$$\Delta h_{O_2} = (29.7 \text{ kJ/g } C_6H_6) \left( \frac{78 \text{ g } C_6H_6}{(5.47)(32 \text{ g } O_2)} \right) = 13.2 \text{ kJ/g } O_2$$

This result illustrates that even for realistic reactions, the  $\Delta h_{O_2}$  appears to remain nearly constant.

Table 2.3 data appear to remain invariant as long as there is sufficient air. By this we mean that with respect to the stoichiometric reaction there is more air than required. In terms of the equivalence ratio, we should have  $\phi < 1$ . When  $\phi$  is zero we have all oxygen and no fuel and when  $\phi = 1$  we have the stoichiometric case with no oxygen or fuel in the products. However, when  $\phi > 1$  we see large departures to the data in Table 2.3. In general,  $CO$  soot and hydrocarbons increase;  $\Delta h_c$  accordingly decrease. Tewarson [3] vividly shows in Figures 2.3 and 2.4 how the  $\Delta h_c$  and the yield of  $CO$  changes for six

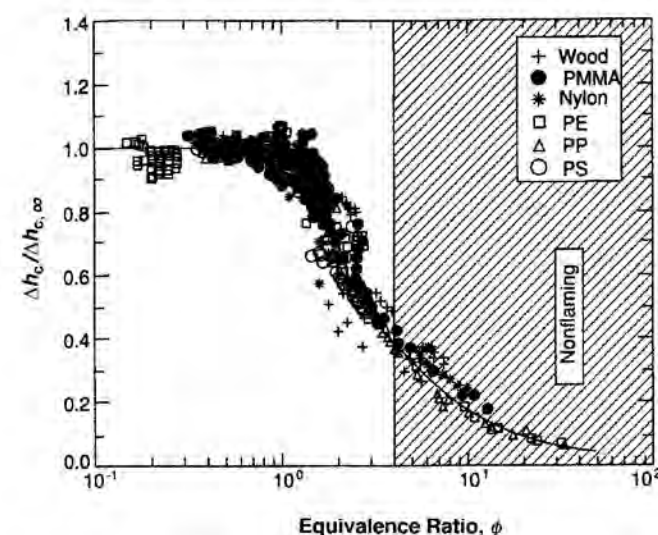


Figure 2.3 Actual heat of combustion in terms of the equivalence ratio where  $\Delta h_{c,\infty}$  is the reference value given in Table 2.3 [3]



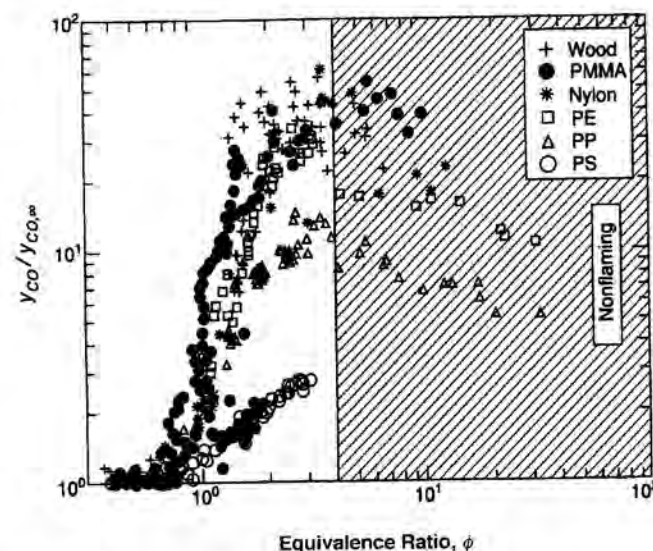


Figure 2.4 Yield of CO in terms of the equivalence ratio where the normalized yield,  $Y_{CO}/Y_{CO,\infty}$ , is given in Table 2.3 [3]

realistic fuels listed in Table 2.3. These results have importance in modeling ventilation-limited fires and determining their toxic hazard. These data are from the FMRC flammability apparatus [3] using the 10 cm  $\times$  10 cm horizontal sample, and for enclosure fires [5].

The flaming results extend to  $\phi = 4$  in Figures 2.3 and 2.4, at which point gas phase combustion appears to cease. However, combustion must continue since the heat of combustion remains nonzero. This is due to oxidation of the remaining solid fuel. If we consider wood, it would be the oxidation of the surface char composed primarily of carbon. From Example 2.3, we obtain the heat of combustion for carbon (going to  $\text{CO}_2$ ) as 32.8 kJ/g carbon. From Figure 2.4, we see a significant production of carbon monoxide at  $\phi = 4$ , and therefore it is understandable that Figure 2.3 yields a lower value:  $\Delta h_c/\Delta h_{c,\infty} = 0.4$  with  $\Delta h_{c,\infty}$  from Table 2.3 of 12.4 kJ/g, or  $\Delta h_c$  at  $\phi = 4$  is 4.96 kJ/g. Here the actual heat of combustion of the char (under nonflaming conditions) at  $\phi = 4$  is 4.96 kJ/g of mass lost while its ideal value is 32.8 kJ/g of carbon reacted. The 'actual' value is not based on stoichiometry of the fuel burned, but on the mass evolved to the gaseous state. The mass evolved may not be equal to the mass of fuel burned.

Therefore, we have shown that thermodynamic principles and properties can be used to describe combustion reactions provided their stoichiometry is known. Since measurements in fire are based on the fuel mass lost, yields are used as empirical properties to describe the reaction and its products. When fire conditions become ventilation-limited ( $\phi \geq 1$ ), the yield properties of a given fuel depend on  $\phi$ . Although the generality of the results typified by Figures 2.3 and 2.4 have not been established, their general trends are accepted.

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4. Huggett, C., Estimation of rate of heat release by means of oxygen consumption, *J. Fire and Flammability*, 1980, **12**, 61-5.
5. Tewarson, A., Jiang, F. H. and Morikawa, T., Ventilation-controlled combustion of polymers, *Combustion and Flame*, 1993, **95**, 151-69.

## Problems

- 2.1 Calculate the vapor densities ( $\text{kg/m}^3$ ) of pure carbon dioxide ( $\text{CO}_2$ ), propane ( $\text{C}_3\text{H}_8$ ) and butane ( $\text{C}_4\text{H}_{10}$ ) at 25 °C and pressure of 1 atm. Assume ideal gas behavior.
- 2.2 Assuming ideal gas behavior, what will be the final volume if 1  $\text{m}^3$  of air is heated from 20 to 700 °C at constant pressure?
- 2.3 Identify the following thermodynamic properties for liquid mixtures:
  - (a) Thermal equilibrium between two systems is given by the equality of \_\_\_\_\_.
  - (b) Mechanical equilibrium between two systems is given by the equality of \_\_\_\_\_.
  - (c) Phase equilibrium between two systems of the same substance is given by the equality of \_\_\_\_\_.
- 2.4 Show that the pressure rise ( $p - p_0$ ) in a closed rigid vessel of volume ( $V$ ) for the net constant heat addition rate ( $\dot{Q}$ ) is

$$\frac{p - p_0}{p_0} = \frac{\dot{Q}t}{\rho_0 V c_v T_0}$$

where  $\rho_0$  is the initial density,  $p_0$  is the initial pressure,  $T_0$  is the initial temperature,  $t$  is time and  $c_v$  is the specific heat at constant volume. The fluid in the vessel is a perfect gas with constant specific heats.

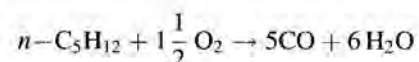
- 2.5 Formaldehyde ( $\text{CH}_2\text{O}$ ) burns to completeness in air. Compute:
  - (a) stoichiometric air to fuel mass ratio;
  - (b) mole fraction of fuel in the reactant mixture for an equivalence ratio ( $\phi$ ) of 2;
  - (c) mole fraction of fuel in the product mixture for  $\phi = 2$ .
- 2.6 Hydrogen reacts with oxygen. Write the balanced stoichiometric chemical equation for the complete reaction.

- 2.7 The mole fraction of argon in a gas mixture with air is 0.1. The mixture is at a pressure of 1000 Pa and 25 °C. What is the partial pressure of the argon?
- 2.8 Compute the enthalpy of formation of propane at 25 °C from its chemical reaction with oxygen and its ideal heat of combustion given in Table 2.3.
- 2.9 Consider the complete stoichiometric reaction for the oxidation of butane:



Calculate the heat of formation using data in Tables 2.2 and 2.3.

- 2.10 Compute the heat transferred in the oxidation of 1 mole of butane to carbon monoxide and water, with reactants and products at 25 °C. Use Table 2.2.



- 2.11 The products for the partial combustion of butane in oxygen were found to contain  $\text{CO}_2$  and  $\text{CO}$  in the ratio of 4:1. What is the actual heat released per mole of butane burned if the only other product is  $\text{H}_2\text{O}$ ? The reactants are at 25 °C and the products achieve 1000 °C. Use average estimates for specific heats. For butane use 320 J/K mole.
- 2.12 Consider heptane burned in air with reactants and products at 25 °C. Compute the heat release per gram of oxygen consumed for (a)  $\text{CO}_2$  formed and (b) only  $\text{CO}$  formed. The other product of combustion is water vapor.
- 2.13 (a) Write the balanced chemical equation for stoichiometric combustion of benzene ( $\text{C}_6\text{H}_6$ ). Assume complete combustion. Calculate the mass of air required to burn a unit mass of combustible.
- (b) For a benzene-air equivalence ratio of 0.75, write the balanced chemical equation and calculate the adiabatic flame temperature in air. The initial temperature is 298 K and pressure is 1 atm. Assume complete combustion.
- (c) Calculate the mole fraction for each product of combustion in part (b).
- (d) Benzene often burns incompletely. If 20 % of the carbon in the benzene is converted to solid carbon and 5 % is being converted to  $\text{CO}$  during combustion, the remainder being converted to  $\text{CO}_2$ , calculate the heat released per gram of oxygen consumed. How does this compare with the value in Table 2.3?
- 2.14 (a) For constant pressure processes show that the net heat released for reactions I and II in succession is the same as for reaction III. The initial and final temperatures are 25 °C. Use data in the text.
- I.  $\text{C}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$
- II.  $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- III.  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- (b) In reaction II, for oxygen in the reactants:
- (i) What is the mole fraction of  $\text{O}_2$ ?

- (ii) What is the mass fraction of  $\text{O}_2$ ?
- (iii) What is the partial pressure of  $\text{O}_2$  if the system pressure is 2 atm.

- 2.15 Carbon monoxide burns in air completely to  $\text{CO}_2$ .
- (a) Write the balanced chemical equation for this reaction.
- (b) Calculate the stoichiometric fuel to air ratio by mass.
- (c) For this reaction, at a constant pressure of 1 atm, with the initial and final temperatures of 25 °C, calculate the change in enthalpy per unit mass of  $\text{CO}$  for a stoichiometric fuel-air mixture.
- (d) What is the quantity in (c) called?
- (e) If the final temperature of this reaction is 500 °C instead, determine the heat lost from the system per unit mass of  $\text{CO}$ .
- (f) Calculate the equivalence ratio for a mixture of five moles of  $\text{CO}$  and seven moles of air. What species would we expect to find in the products other than  $\text{CO}_2$ ?
- 2.16 Determine the heat of combustion of toluene and express it in proper thermodynamic form. The heat of formation is 11.95 kcal/mole.
- 2.17 Hydrogen stoichiometrically burns in oxygen to form water vapor. Let  $c_{p,i} = 1.5 \text{ J/g K}$  for all species.
- (a) For a reaction at 25 °C, the enthalpy change of the system per unit mass of  $\text{H}_2$  is called \_\_\_\_\_.
- (b) For a reaction at 25 °C, the enthalpy change of the system per unit mass of  $\text{H}_2\text{O}$  is called \_\_\_\_\_.
- (c) Compute the enthalpy change of the system per unit mass of water vapor at 1000 °C.
- (d) The initial temperature is 25 °C and the temperature after the reaction is 1000 °C. Compute the heat transfer for the system per unit mass of  $\text{H}_2$  burned. Is this lost or added?
- (e) Repeat (d) for an initial temperature of 300 °C.
- 2.18 Compute the heat of combustion per gram mole of acetonitrile.

Acetonitrile ( $\text{C}_2\text{H}_3\text{N}_{(\text{g})}$ ) burns to form hydrogen cyanide ( $\text{HCN}_{(\text{g})}$ ), carbon dioxide and water vapor.

Heat of formation in kcal/gmol

Hydrogen cyanide:	32.3
Acetonitrile:	21.0
Water vapor:	-57.8
Carbon dioxide:	-94.1
Oxygen:	0.0

- 2.19 An experimentalist assumes that, when wood burns, it can be approximated by producing gaseous fuel in the form of formaldehyde and char in the form of carbon.

## Heat of formation in kcal/gmol

Formaldehyde (CH <sub>2</sub> O):	-27.7
Carbon (C):	0
Oxygen (O <sub>2</sub> ):	0
Nitrogen (N <sub>2</sub> ):	0
Water vapor (H <sub>2</sub> O):	-57.8
Carbon dioxide (CO <sub>2</sub> ):	-94.1

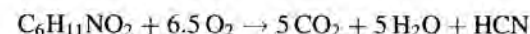
Assume complete combustion in the following:

- Compute the heat of combustion of CH<sub>2</sub>O in kJ/kg.
  - Compute the heat of combustion of C in kJ/kg.
  - What heat of combustion would an engineer use to estimate the energy release of wood during flaming combustion?
  - The char yield of wood is 0.1 g C/g wood. Compute the heat of combustion of the solid wood after all of the char completely oxidizes, in kJ/g of wood.
- 2.20 Determine by calculation the enthalpy of formation in kJ/mole of CH<sub>4</sub> given that its heat of combustion is 50.0 kJ/g at 25 °C. The heat of formation for carbon dioxide is -394 kJ/mole and water vapor is -242 kJ/mole.
- 2.21 Nylon (C<sub>6</sub>H<sub>11</sub>NO) burns as a gas in air. There is 8 times the amount of stoichiometric air available by moles. The reaction takes place at constant pressure. The initial fuel temperature is 300 °C and the air is at 25 °C. The reaction produces CO<sub>2</sub>, H<sub>2</sub>O (gas) and HCN in the molar ratio, HCN/CO<sub>2</sub> = 1/5.

Other properties: Heat of formation of nylon = -135 kJ/mole

Species	Molar specific heats at constant pressure (J/K mole)
Nylon (gas)	136
H <sub>2</sub> O	50
CO <sub>2</sub>	60
HCN	90
N <sub>2</sub>	35
O <sub>2</sub>	35

- Compute the heat of combustion for this reaction using data in Table 2.2.
  - Compute the temperature of the final state of the products for an adiabatic process.
- 2.22 Nylon burns to form carbon dioxide, water vapor and hydrogen cyanide, as shown in the stoichiometric equation below:



The heat of combustion of nylon is 30.8 kJ/g. Find the heat of formation of the nylon in kJ/mole.

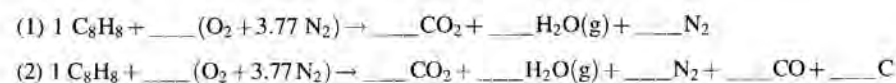
- 2.23 Neoprene (C<sub>4</sub>H<sub>5</sub>Cl) is burned in air at constant pressure with the reactants and products at 25 °C. The mass yields of some species are found by measurement in terms of g/g<sub>F</sub>. These product yields are CO at 0.1, soot (taken as pure carbon, C) at 0.1 and gaseous unburned hydrocarbons (represented as benzene, C<sub>6</sub>H<sub>6</sub>) at 0.03. The remaining products are water as a gas, carbon dioxide and gaseous hydrogen chloride (HCl).

- Write the chemical equation with molar stoichiometric coefficients, taking air as 1 mole of O<sub>2</sub> + 3.77 moles of N<sub>2</sub> (i.e. 4.77 moles of air).
- Calculate the heat of formation of the neoprene (in kJ/mole) if it is known that the heat of combustion for reaction (a) is 11 kJ/g neoprene.
- If the reaction were complete to only stable gaseous products, namely water vapor, carbon dioxide and chlorine (Cl<sub>2</sub>), compute the heat of combustion in kJ/g.
- For both reactions (a) and (c), compute the energy release per unit mass of oxygen consumed, i.e.  $[H(\text{reactants}) - H(\text{products})]/\text{mass of oxygen}$ .

Atomic weights: C,12; H,1; O,16; N,14; Cl,35.5, and use Table 2.2.

- 2.24 Formaldehyde is stoichiometrically burned at constant pressure with oxygen (gas) to completion. CO<sub>2</sub> and H<sub>2</sub>O, condensed as a liquid, are the sole products. The initial temperature before the reaction is 50 °C and the final temperature after its completion is 600 °C. Find, per mole of fuel, the heat transferred in the process, and state whether it is added or lost. Assume a constant specific heat of 35 J/mole K for all the species. Use Table 2.2 for all of your data.
- 2.25 The heat of combustion for the reaction times the mass of fuel reacted is equal to:
- the chemical energy released due to realignment of the molecular structures;
  - the heat lost when the reactants and the products are at 25 °C;
  - the chemical energy when the fuel concentration in the reactants is at the upper flammable limit.
- 2.26 Cane sugar, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, reacts with oxygen to form char, gaseous water and carbon dioxide. Two moles of char are formed per mole of sugar cane. Assume the char is pure carbon (graphite). Compute the heat of combustion on a mass basis (kJ/g) for the sugar cane in this reaction. The heat of formation of the sugar cane is -2220 kJ/mole. Cite any data taken from Tables 2.1 and 2.2.
- 2.27 Hydrogen gas (H<sub>2</sub>) reacts completely with air in a combustor to form water vapor with no excess air. The combustor is at steady state. If the flow rate of the hydrogen is 1 kg/s, what is the heat transfer rate to or from the combustor? The heat of combustion of hydrogen gas is 121 kJ/g, the initial temperature of the air and hydrogen is 600 K and the exiting temperature of the gases leaving the combustor is 3000 K. Assume constant and equal specific heats of constant pressure, 1.25 kJ/kg K. Show all work, diagrams and reasoning, and indicate whether the heat is from or to the combustor wall.
- 2.28 Polystyrene can be represented as C<sub>8</sub>H<sub>8</sub>. Its heat of combustion for a *complete* reaction to carbon dioxide and water vapor is 4077 kJ/mole.
- Compute the heat of formation of C<sub>8</sub>H<sub>8</sub> in kJ/mole.
  - Compute the heat of combustion of C<sub>8</sub>H<sub>8</sub> in kJ/g for the *incomplete* reaction in air with water vapor in the products as shown below:
- $$\text{C}_8\text{H}_8 + \left(\frac{17}{2}\right) [\text{O}_2 + 3.77 \text{N}_2] \rightarrow 6 \text{CO}_2 + \text{CO} + \text{C} + 4 \text{H}_2\text{O} + \left(\frac{17}{2}\right) (3.77) \text{N}_2$$
- 2.29 Polystyrene (C<sub>8</sub>H<sub>8</sub>)<sub>n</sub> reacts with the oxygen in air; 4.77 moles of air can be represented as O<sub>2</sub> + 3.77 N<sub>2</sub>.





For the incomplete reaction, (2), the molar ratios of the incomplete products are given as

$$\text{CO} / \text{CO}_2 = 0.07 \text{ and } \text{C} / \text{CO}_2 = 0.10$$

- Balance each chemical equation.
- Compute the heat of combustion for each, on a mass basis.
- Compute the heat of combustion per unit mass of oxygen used for each reaction.
- Compute the adiabatic flame temperature for each.
- Compute the adiabatic flame temperature for each reaction in pure oxygen.

Use the information in the chapter 2 to work the problem. You can assume constant specific heats of the species at an appropriate mean temperature (use 1600 K). Also, the heat of formation of polystyrene is  $-38.4 \text{ kJ/mole}$ .

- 2.30 (a) Determine the heat of combustion of ethylene,  $\text{C}_2\text{H}_4$ , for a complete reaction to carbon dioxide and water vapor.
- (b) Determine its adiabatic flame temperature for a complete reaction with pure oxygen. Assume again water vapor in the products. Use information in Tables 2.1 and 2.2.
- 2.31 Calculate the adiabatic flame temperatures for the following mixtures initially at  $25^\circ\text{C}$ :
- stoichiometric butane-oxygen mixture;
  - stoichiometric butane-air mixture;
  - 1.8 % butane in air.

Use specific heat values of  $250 \text{ J/K mole}$  for butane and  $36 \text{ J/K mole}$  for oxygen and nitrogen.

- 2.32 Calculate the adiabatic flame temperature (at constant pressure) for ethane  $\text{C}_2\text{H}_6$  in air:
- at the lower flammability limit ( $X_L = 3.0\%$ ) and
  - at the stoichiometric mixture condition.

Assume constant specific heats for all species ( $1.1 \text{ kJ/kg K}$ ) and use the data from Tables 2.3 and 4.5. The initial state is  $1 \text{ atm}$ ,  $25^\circ\text{C}$  and the initial mixture density is  $1.2 \text{ kg/m}^3$ .

- 2.33 A gaseous mixture of 2 % (by volume) acetone and 4 % ethanol in air is at  $25^\circ\text{C}$  and a pressure of  $1 \text{ atm}$ .

#### Data

Acetone ( $\text{C}_3\text{H}_6\text{O}$ ) has  $\Delta h_c = 1786 \text{ kJ/g mol}$

Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) has  $\Delta h_c = 1232 \text{ kJ/g mol}$

Atomic weights:  $\text{H} = 1 \text{ mole}$ ,  $\text{C} = 12 \text{ moles}$ ,  $\text{O} = 16 \text{ moles}$  and  $\text{N} = 14 \text{ moles}$

Specific heats,  $c_{p,i} = 1 \text{ kJ/kg K}$ , constant for each species

- For a constant pressure reaction, calculate the partial pressure of the oxygen in the product mixture.

- Determine the adiabatic flame temperature of this mixture.
- If this mixture was initially at  $400^\circ\text{C}$ , what will the resultant adiabatic flame temperature be?

- 2.34 Polyacrylonitrile ( $\text{C}_3\text{H}_3\text{N}$ ) burns to form vapor, carbon dioxide and nitrogen. The heat of formation of the polyacrylonitrile is  $+15.85 \text{ kcal/g mol}$  ( $1 \text{ cal} = 4.186 \text{ kJ}$ ). Use data from Tables 2.1 and 2.2; use specific heat values at  $1000 \text{ K}$ .

- Write the balanced chemical equation for the stoichiometric combustion in oxygen.
- Determine the heat of combustion of the polyacrylonitrile.
- Write the balanced chemical equation for the stoichiometric combustion in air.
- Determine the adiabatic flame temperature if the fuel burns stoichiometrically in air.

- 2.35 Toluene ( $\text{C}_7\text{H}_8$ ) as a gas burns stoichiometrically in air to completion (i.e. forming carbon dioxide and water vapor).

#### Data

Heat of formation of toluene is  $+11.95 \text{ kcal/g mol}$

Species	Specific heat (cal/g mol K) at $1500 \text{ K}$
Oxygen	8.74
Water (gas)	11.1
Carbon dioxide	14.0

- For products and reactants at  $25^\circ\text{C}$ , compute the heat loss per unit gram mole of toluene consumed.
- What is the quantity in (a) called?
- For reactants at  $25^\circ\text{C}$ , compute the adiabatic flame temperature.

- 2.36 Check all correct answers below:

- For reacting systems, the conservation of mass implies:
  - the preservation of atoms,
  - the conservation of moles,
  - the conservation of molecules,
  - the conservation of species,
  - the equality of mass for the reactants and products in a closed system.
- Stoichiometric coefficients represent:
  - the number of molecules for each species in the reaction,
  - the number of moles for each species in the reaction,
  - the number of atoms for each species in the reaction,
  - the number of grams for each species in the reaction,
  - the number before the chemical species formulas in a balanced chemical equation.