11.1 The Combustion Continuum
11.2 Aspects of Combustion
11.3 Fires and Flames
11.4 Arson and Fire Investigation

OVERVIEW AND ORIENTATION

The next few chapters will tackle the second most important work area (behind drug analysis and toxicology) in forensic chemistry. We will begin with an exploration of the fundamentals of combustion, a specialized type of oxidation–reduction that spans candle flames to powerful and destructive explosions. The important differences between a fire and a bomb are the speed at which the combustion occurs and the degree to which it is confined. As we will see, combustion can be thought of as a continuum. Forensically, combustion is the process at the heart of arson, bombing, and, perhaps less obviously, gunshot residue. In this chapter, we will cover the fundamental principles that underlie these three types of forensic cases and evidence and discuss the physical evidence associated with fires. In Chapter 12, we will delve into propellants and gunshot residue and complete our discussion in Chapter 13, where we will explore explosives.

11.1 THE COMBUSTION CONTINUUM

Combustion is an oxidative decomposition in which oxygen (the oxidant) oxidizes a fuel. The different manifestations of combustion (Figure 11.1), ranging from a gentle candle flame to a violent military explosive, are part of a continuum that includes the propellants used in firearms. The terms we use to describe this decomposition depends on characteristics such as the speed of the reaction. For example, in the detonation of an explosive, the reaction front moves faster than the speed of sound (~ 741 mph, or 331 m/s). If this same reaction occurs at less than the speed of sound, it is called deflagration. This term can also be applied to what we mean by the term “burning,” in which the flame speed is less than the speed of sound. As the flame front’s speed increases, oxygen from the atmosphere is incapable of sustaining it, and additional oxygen must come from another source such as potassium nitrate (KNO₃, or saltpeter). The fuel must also change as the energy derived from it increases.

The Chemistry of Combustion and Arson

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Combustion is an exothermic reaction in which reactants are converted to principally gaseous products. Because the reaction is exothermic, the product gases heat up and expand, and in turn can be harnessed to do work. In a fire, such as arson, this expansion generates plumes with predictable behaviors that leave distinctive markings at the crime scene. In contrast, the expansion of hot gases is utilized in propellants to drive a projectile forward (pressure–volume, or $PV$ work), whereas in explosives the expanding gases are confined as long as possible to generate a destructive shock wave. Because of this confinement, a detonation is a mechanical process, whereas deflagration is a thermal one. This critical distinction will be discussed in detail in the next section.

<table>
<thead>
<tr>
<th>Burning/Flame/Deflagration</th>
<th>Explosion/Detonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forensic application</td>
<td>Arson fire investigation</td>
</tr>
<tr>
<td>Speed of burn</td>
<td>Subsonic</td>
</tr>
<tr>
<td></td>
<td>Slow</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel</td>
<td>Hydrocarbons</td>
</tr>
<tr>
<td></td>
<td>C═H, H═H</td>
</tr>
<tr>
<td></td>
<td>C═N</td>
</tr>
<tr>
<td>Oxidant</td>
<td>$O_2$(air)</td>
</tr>
<tr>
<td></td>
<td>$KNO_3$</td>
</tr>
<tr>
<td></td>
<td>(Nitrate carbohydrates)</td>
</tr>
<tr>
<td>Confinement pressure</td>
<td>Unconfined/low</td>
</tr>
<tr>
<td></td>
<td>Confined/high</td>
</tr>
<tr>
<td>Type of initiation process</td>
<td>Thermal</td>
</tr>
<tr>
<td>Range of effects</td>
<td>Generalized</td>
</tr>
<tr>
<td></td>
<td>Localized</td>
</tr>
</tbody>
</table>

**FIGURE 11.1** The continuum of combustion. The dividing line between burning, deflagration, and detonation is the speed at which the reaction front propagates.

Combustion is an exothermic reaction in which reactants are converted to principally gaseous products. Because the reaction is exothermic, the product gases heat up and expand, and in turn can be harnessed to do work. In a fire, such as arson, this expansion generates plumes with predictable behaviors that leave distinctive markings at the crime scene. In contrast, the expansion of hot gases is utilized in propellants to drive a projectile forward (pressure–volume, or $PV$ work), whereas in explosives the expanding gases are confined as long as possible to generate a destructive shock wave. Because of this confinement, a detonation is a mechanical process, whereas deflagration is a thermal one. This critical distinction will be discussed in detail in the next section.

**EXHIBIT A**

Salt, Peter?

An older name for the salt $KNO_3$ (potassium nitrate) is saltpeter (also spelled salt Peter and salt peter), which is used as a chemical oxidant in gunpowder and explosives. Saltpeter is a mineral that forms when organic material such as waste, decaying plants, and animal manure is placed in contact with soil high in alkali content (such as limestone). Saltpeter is found on the earth’s
Combustion requires reactants and enough energy to exceed the energy of activation ($E_a$) required to initiate the reaction. The reaction profile shown in Figure 11.2 illustrates the exothermic nature of a combustion reaction, as well as the need for enough energy to initiate it. Once initiated, enough energy is produced to supply the necessary $E_a$ to sustain the reaction until one of the reactants is exhausted. With a simple flame, the fuel is exhausted first, since the oxidant is atmospheric oxygen. When chemical oxidants are employed, either fuel or oxidant may be the limiting reagent.

The energy released in a combustion reaction results from the increased stability (lower potential energy) of the products relative to that of the reactants. The energy ($\Delta H$) released can be estimated with the two methods shown in Figure 11.3. The first method is based on table values (found in Appendix 5) of thermodynamic quantities under standard conditions of temperature and pressure (STP, 25°C and 1 atm). The second method calculates how much energy is required to break the chemical bonds in the reactants and form the bonds of the products. As shown in the figure, this result should be relatively close to that determined from the table values; however, the quantities calculated are used only as starting points, because the combustion reactions encountered in forensic chemistry are complex and rarely occur close to standard conditions. Even if the reaction starts at near standard conditions, the reaction itself quickly pushes the system well beyond standard conditions.

Some readers may be familiar with the fire triangle, which is one way of summarizing the requirements for a combustion reaction. Such a triangle is divided into three regions, identified as fuel, oxidant, and heat (the last of which supplies $E_a$). Building on the concept of the triangle, we will consider the requirements for combustion to be

1. fuel and oxidant in proper quantities and concentrations,
2. a source of $E_a$, and
3. sufficient contact time for the energy source to initiate the reaction.

The absence of any one factor prevents combustion. We will examine the particulars of each factor next.

The first requirement, fuel and oxidant in proper proportions, illustrates key points and unmasks common misconceptions. Wood does not burn; rather, what burns are the vapors emanating from heated wood. Gasoline in a can will not explode because the proper fuel–air mixture does not exist. A cigarette tossed into a pool of gasoline usually smothers before it has a chance to ignite the vapor above it. Similarly, the Hollywood staple of exploding gas tanks in cars is more fiction than fact. Rapid burning can occur, but only when the gas tank is ruptured, the contents leak and vaporize, and the proper air–fuel vapor mixture is created at the same time and place as a source of ignition that stays in contact long enough to spark the reaction.

### 11.2 ASPECTS OF COMBUSTION

Consider a simple model of combustion: burning wood (Figure 11.4). Once the fire is burning, heat must be transferred efficiently to the wood to vaporize reactants. Heat transfer is also needed to ensure that $E_a$ is overcome and the reaction is self-sustaining. Specifically, the activation energy must be sufficient to form free radicals, the heart of combustion reaction mechanisms. Oxygen must move into the reaction zone via mass transfer, and the rate of this transfer directly affects the reaction. Think of blowing across a smoldering fire, an action that increases the efficiency of mass transport of oxygen and speeds the reaction by supplying more oxidizing agent. The kinetics
Part IV • Combustion Evidence

(speed) of combustion depends on the rate of formation of free radicals in the flame flickering above the wood. The reaction speed also depends on multiple rate constants and reactant concentrations in multiple connected chain-reaction pathways. The heat evolved, favored pathways, and the balance of products will all depend on thermodynamic considerations, including stoichiometric ratios and equilibria. Thus, although we will address each of these topics individually, all interact to control and define the complex process of combustion.

11.2.1 Thermodynamics

Thermodynamics relates concepts of energy flow, enthalpy ($H$), entropy ($S$), free energy ($G$), and equilibrium. The first law of thermodynamics states roughly that energy is neither created nor destroyed but only changes form. In combustion and in explosions, potential energy in chemical bonds (chemical energy) is converted to heat and

---

*Equilibrium is defined as the point at which $\Delta G = 0$.\(^1\)
work. Energy is defined as the ability to do work and can be categorized by the type of work done. For example, there is chemical energy, potential energy, mechanical energy, and kinetic energy. The second law of thermodynamics relates to entropy and (again, roughly) states that in any spontaneous process, the disorder of the universe increases. Entropy increases during combustion because gaseous products are formed and heat is released by the exothermic reaction. Molecules move faster at higher temperatures relative to molecules at lower temperatures, resulting in increased disorder.

The free-energy change of any reaction, including combustion, is defined in terms of enthalpy and entropy:

\[ \Delta G = \Delta H - T\Delta S \]  \hspace{1cm} (11.1)

where \( S \) is entropy and \( G \) is the Gibbs free energy. In a flame, the combination of an exothermic reaction with increasing disorder leads to a large negative value for the change in free energy (\( \Delta G \)). \( \Delta G \) also is a measure of how much work can be done by a system in a spontaneous reaction. Work can be divided into two components: actual work (\( w \)) and heat (\( q \)). Both aspects come into play across the combustion continuum. In a fire, such as an intentionally set arson fire, heat and gases are produced but are not exploited to do work. In propellants and explosives, heat and work play critical roles and the work done is the central issue.

In chemical applications, the most common type of work is \( PV \) work. Examples are shown in Figure 11.5. The top frame illustrates how the evolution of a gas (H\(_2\)) in a spontaneous process is used to do \( PV \) work in a system in which heat is a minor contributor. The lower frame depicts the relationship between \( PV \), work, and force. To move the piston, work—specifically, \( PV \) work—must be done, and the force acting inside the cylinder must exceed the force exerted by atmospheric pressure. If the piston was removed from the system, the gasoline would still ignite, burn, and generate hot expanding gases; however, this expansion is not purposely directed into doing \( PV \) work. This is the situation we see in arson fires.

Forensic examples involving energy and illustrating how work is done are shown in Figures 11.6 and 11.7. In Figure 11.6, a bullet is propelled out of a gun by \( PV \) work done by expanding gases produced by the burning propellant. Here, the bullet is analogous to the piston (Figure 11.5), which is moved as a result of the production of gas. In the gun, primer ignites when struck by the hammer, provides the initial \( E_s \) spark, and initiates combustion, which produces heat and hot expanding gases. The bullet is held in the cartridge by compression and friction, but the joint is designed to give way once sufficient pressure builds up. The result is movement of the bullet down the barrel, just like movement of the piston shown in Figure 11.5, except that the force must overcome the compression and friction forces holding the bullet in place. As gas expansion continues, much of the energy is transferred to the bullet as kinetic energy. The energy trace of a gun firing can be summarized as a mechanical energy (hammer striking primer) \( \rightarrow \) chemical energy \( \rightarrow \) heat and work (heat and mechanical) \( \rightarrow \) kinetic energy. This progression can be simplified to ME \( \rightarrow \) CE \( \rightarrow \) ME (and heat) \( \rightarrow \) KE.

For a crude pipe bomb (Figure 11.7) made of galvanized steel pipe and gunpowder, the energy pathway is the same. What differs is that no joint is designed to fail, as was the case with the gun firing. A pipe bomb is a mechanically stronger containment device that allows pressure to build until it exceeds the strength of the container at its weakest point. As we will see in Chapter 13, pressure and confinement are critical factors in explosions and detonations. The pipe shatters and ejects shrapnel in all directions. In contrast, a gun is designed to focus and direct the gas expansion and work in order to impart the most kinetic energy to a single projectile traveling in a controlled trajectory in one direction.
FIGURE 11.5 Two illustrations of PV work. In the top frame, zinc metal is dropped into acid, and pressure exerted by the evolving gas raises the piston. In the lower frame, pressure is defined as force per unit area (F/A), but the concept is the same and the $P\Delta V$ term can be calculated geometrically by using the volume of a cylinder. For the piston to move, work of quantity $-P\Delta V$ must be done by the system. An example of this mechanism is gasoline burning in the cylinder of an internal combustion engine.

FIGURE 11.6 How a combustion reaction is used to create sufficient energy to do the work of moving a bullet out of a gun barrel.
Before going further, we should introduce terminology to eliminate the negative–positive sign confusion often associated with the heat of reaction and the release of heat. All of the combustion reactions we will deal with in this chapter are exothermic, all release heat, and all have a negative value for $\Delta H^\circ_{\text{reaction}}$. The heat released by the system is absorbed by the surroundings and is always positive. In the examples just discussed, the system is the burning propellant or the detonating explosive. These reactions release heat to the surroundings, such as the gun barrel. For this discussion, heat released will be referred to as $Q$, in keeping with traditional thermochemical notation. In combustion, $Q$ is always positive and numerically the opposite of $\Delta H^\circ_{\text{reaction}}$:

$$Q = -(\Delta H^\circ_{\text{reaction}})$$  \hfill (11.2)

We will also assume that combustion is \textit{adiabatic combustion}—that is, that the heat released is used only to heat the products and that there is no heat exchange to the surroundings. Again, using the gun example, if the firing process is adiabatic, it means that all the heat evolved is consumed by heating of the products created by the combustion reaction. Of course, this is only an approximation, but a useful one.

Heating the products also increases their kinetic energy. This heating causes pressure to increase, according to the ideal gas law:

$$PV = nRT$$  \hfill (11.3)

This law shows that temperature is directly proportional to pressure and volume. In the case of an explosive, the higher the pressure generated, the more powerful is the explosive. The power of an explosive can be defined as $VQ$, where $V$ is the volume of gaseous products and $Q$ is the heat evolved.\cite{1} Thus, the most powerful explosives (per gram) are those that create the largest number of moles ($n$) of gas at the highest temperatures. A common way to express this relationship is via a modification of the ideal-gas law:\cite{1}

$$F = nRT_e$$  \hfill (11.4)

where $F$ is force of the explosive, $n$ is number of moles of gas produced, and $T_e$ is the temperature of the resulting product mix.

\[\text{FIGURE 11.7} \quad \text{A pipe bomb is designed to rupture and not to fail at a specific joint. The result is catastrophic destruction of the container and the ejection of sharp shrapnel moving at high speed.}\]
The value of \( Q \) (used to heat the products to \( T_e \)) is central to describing and estimating explosive power. Figure 11.3 illustrated two methods of calculation of the heat of reaction, but of more interest here is gauging the relative heat generated per gram of fuel. Also, the calculations shown in Figure 11.3 assume that the fuel and oxidant are in **stoichiometric equivalence** (which we abbreviate as STE), meaning that the molar amounts of fuel and oxidant are in exactly the correct proportions according to the balanced equation for the reaction to go to completion. In the case of methane combustion (Figure 11.2), if 1.0 mol of methane was present when the reaction started, then at STE there would be exactly 2.0 mol of \( O_2 \) present. This situation, however, is rarely encountered, and as a result, both the products of the reaction and the heat evolved will be affected.

**EXAMPLE PROBLEM 11.1**

Assuming that conditions are such that methane (CH\(_4\)) and methanol (CH\(_3\)OH) combust via an explosion, which is the more powerful per gram detonated?

**Answer:**

To answer this question, the value of heat released (\( Q \) or \( \Delta H \)) for each compound is needed, as well as the number of moles of gas produced. Use the thermodynamic values provided in Appendix 5 to determine \( Q \) per mole combusted. Some assumptions are necessary, but for a rough comparison, this approach is reasonable. Here, we will treat all species in the gas phase.

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)
\]

\[
\begin{array}{ccc}
\Delta H_g & -74.8 & -393.5 & -241.82 \\
n_{\text{mol}} & 1.0 & 1.0 & 2.0 \\
n_{\text{grams}} & 1.0 & & \\
n_{\text{moles/gram}} & 0.063 & 0.063 & 0.125 \quad (0.19 \text{ total moles per gram}) \\
\end{array}
\]

\[
\Delta H_{\text{reaction}} = [-393.5 + 2(-241.82)] - (-74.8) = \frac{50.1 \text{ kJ}}{\text{mol CH}_4} = \frac{50 \text{ kJ}}{\text{g CH}_4}
\]

\[
2\text{CH}_3\text{OH}(g) + 3\text{O}_2 \rightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(g)
\]

\[
\begin{array}{l}
\text{2 mol} ightarrow 6 \text{ mol gas} \\
\text{moles/gram} \, 0.0313 \rightarrow 0.0313 \text{ mol} + 0.0625 \text{ mol or, calculated as above,}\frac{2.1 \text{ L}}{\text{g CH}_3\text{OH}}
\end{array}
\]

\[
\Delta H_{\text{reaction}}^o = \frac{-1069 \text{ kJ}}{2 \text{ mol CH}_3\text{OH}} = \frac{-535 \text{ kJ}}{\text{mol CH}_3\text{OH}} = \frac{16 \text{ kJ}}{\text{g CH}_3\text{OH}}
\]

\[
QV_{\text{CH}_4} \equiv 50 \times 4.3 \equiv 215 \quad QV_{\text{CH}_3\text{OH}} = (16)(2.1) = 33
\]

The difference is \( \sim \) a factor of 6 for 1 g of each substance.

Notice that, in balancing the equations, clearing the fractions was not necessary, since the oxygen does not contribute to \( Q \). The combustion of a gram of methanol produces about half the gas volume of the combustion of a gram of methane. Thus, ethanol is a better fuel, at least using this one metric.
Using the ratio of fuel to air at STE as a reference point, we can describe situations in which we do not have STE. When the amount of fuel relative to the amount of oxidant decreases, the mixture becomes a \textit{lean mixture}. In chemical terms, the system is overoxidized, and if the fuel concentration drops too low relative to the concentration of oxidant, combustion cannot take place. When there is more fuel relative to the oxidant, the mixture is \textit{rich}, and the system is underoxidized. At the extreme of richness, combustion is impossible. An underoxidized system favors production of the less oxidized product and releases less heat.

The calculation of the \textit{fuel/air ratio} (F/A) is an important one and can assist in determining such properties as potential flammability of mixtures. Returning to the combustion of methane as our example, the molar ratio of methane to oxygen in a balanced equation at STE is 1:2, respectively. Because the types of combustion of interest here take place in air, additional corrections are required. Assuming that the atmosphere is 21% oxygen, the number of moles of air supplied must be adjusted upward. A mole of air contains 0.21 mol of \( O_2 \); to obtain 1 mol of \( O_2 \), we need to multiply this value by \( 4.76 \times 0.21 = 1.0 \). One last adjustment is to multiply this result by 2, since the complete combustion of 1 mol of methane requires 2 mol of oxygen. This value is easily converted to a mass ratio using the formula weight of methane (16.0 g/mol) and the weighted average mass of air, which is generally taken to be 28.85 g/mol:

\[
F/A = \frac{(16.0 \text{ g/mol})(1 \text{ mol})}{(2.0 \text{ mol } O_2)(4.76 \text{ mol air})/1 \text{ mol } O_2} = \frac{28.85 \text{ g}}{1 \text{ mol air}} = 0.0583 \tag{11.5}
\]

Thus, at stoichiometric equivalence, the mass ratio F/A is 0.0583. It is important to note that here we are assuming a closed system, in that the fuel and air are being held at a fixed volume at 1.0 atm. We will see many instances in which we have to make some basic assumptions about conditions, and in many cases, our calculations are reasonable estimates, not hard values. However, these types of calculations are the foundations of complex models used to describe combustion, deflagration, and detonation.

Now, consider an example in which 5.0 g of methane is released into a container of air with a volume of 20.0 L at a temperature of 25°C. To determine whether the resulting mixture is combustible, rich, or lean, the mass ratios of fuel to air are calculated and compared with the ratio at STE just calculated. The first step is to obtain mole ratios via partial pressures and the ideal gas law:

\[
\frac{n_{CH_4}RT}{V} = \frac{5.0 \text{ g}}{16.0 \text{ g/mol}} \times \frac{0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K}}{298 \text{ K}} \times \frac{298 \text{ K}}{20.0 \text{ L}} = 0.38 \tag{11.6}
\]

Therefore, \( P_{\text{air}} = 0.62 \)

We convert these mole fractions to mass using formula weights:

\[
M_{\text{CH}_4} = M_F = (0.38 \text{ mol})(16.0 \text{ g/mol}) = 6.1 \text{ g} \tag{11.7}
\]

\[
M_{\text{air}} = 0.62 \text{ mol}(28.85 \text{ g/mol}) = 18.0 \text{ g}
\]

The last step is to determine the F/A ratio relative to that at STE:

\[
\frac{(M_F/M_A)_{\text{SYS}}}{0.0583} = \frac{6.1 \text{ g}}{18.0 \text{ g}} = 5.8 \tag{11.8}
\]
The mixture in the container is rich relative to the STE ratio. As seen in Figure 11.8, deviations from STE affect the temperature of the flame; we will see why momentarily.

Staying with our methane example, Figure 11.8 illustrates how rich and lean mixtures alter the heat evolved. The heat released at stoichiometric equivalence was previously calculated (Figure 11.3); note that the heats of formation for water (in gas or liquid form) and methane are constants in this combustion, and the contribution of elemental O₂ is zero. As a result, the expression for calculating $\Delta H^o$ to compare the three reactions depicted in the figure can be simplified as follows:

$$\Delta H^o_{\text{reaction}} = X_{\text{CO}} \Delta H^o_{\text{CO(g)}} + X_{\text{CO}_2} \Delta H^o_{\text{CO}_2(g)}}$$  \hfill (11.9)
$$\Delta H^o_{\text{reaction}} = X_{\text{CO}}(-110.5 \text{ kJ/mol}) + X_{\text{CO}_2}(-393.5 \text{ kJ/mol})$$  \hfill (11.10)

where $X_i$ represents the mole fraction of each species produced. The most negative value (the largest $Q$) occurs when only CO₂ is produced. Any carbon monoxide pro-
duced decreases the heat released, since the overall heat of the reaction becomes more positive (ΔH°_reaction becomes less negative). Thus, underoxidized systems, which favor CO production, release less heat than do systems at stoichiometric equivalence. However, if there is excess oxidant, some of the heat evolved is diverted to heat that oxidant, rather than just the products, as we assumed in the adiabatic combustion model. As a result of heat diversion, Q decreases from the maximum produced at stoichiometric equivalence, at which Q heats only the products.

The discussion becomes more interesting when we examine reactions in which the oxidant is not atmospheric oxygen or in which the source of oxygen is chemical, as in the case of explosives such as TNT or nitroglycerin (Figure 11.10). With these explosives, part of the oxidant is supplied by the molecule, part is supplied by the atmosphere, and the ratio is expressed as the oxygen balance. As demonstrated in Example Problem 11.3, nitroglycerin has a positive oxygen balance, meaning that when the explosive decomposes to gaseous products, the explosive molecule itself can supply all the needed oxygen, with some to spare. The reverse is true for explosives such as TNT, which require oxygen from the atmosphere or another chemical source. When the oxygen balance is negative and relatively large, CO will form in preference to CO₂. In other words, the system is underoxidized and lean. The oxygen balance can also be expressed as a weight-percentage-like quantity derived from the ratio

$$\text{Mass O released or consumed} \over \text{Mass of explosive}$$

(11.11)

**EXAMPLE PROBLEM 11.2**

For combustion of a hydrocarbon such as methane or ethane, is the oxygen balance positive or negative?

*Answer:* The oxygen balance is always negative. There is no oxygen in the molecule.

Example Problem 11.3 illustrates how oxygen balance is calculated, and Table 11.1 gives the oxygen balance of some representative explosives.

The concept of oxygen balance is analogous to the definition of a rich or lean mixture of fuel versus oxidant. The difference is that the oxygen balance is internal

<table>
<thead>
<tr>
<th>Explosive</th>
<th>Oxygen Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium nitrate</td>
<td>+20%</td>
</tr>
<tr>
<td>Nitroglycerin</td>
<td>+4</td>
</tr>
<tr>
<td>Picric acid</td>
<td>-45</td>
</tr>
<tr>
<td>TNT</td>
<td>-74</td>
</tr>
</tbody>
</table>

**FIGURE 11.10** Two common explosives.
Applying the Science 11.1

It is not unheard of for fires to be set with the intent of destroying evidence of other crimes such as murder. A recent study addressed how fires affect blood evidence – both detection of bloodstain patterns and the ability to obtain typable DNA samples from blood after a fire. In this project, fires were set under tightly controlled conditions after bloodstains had purposely created in several rooms in the structure. Postfire, analysts studied the performance of reagents used for presumptive testing of blood including phenolphthalein, luminol and fluorescein on the stains, most of which remained visible even after burning. Results were generally poor, although some positives were obtained. The authors correlated maximum temperatures with the ability to obtain full and partial DNA profiles and found that in areas where the temperature exceeded 923°C, they obtained full profiles from about a third of the samples, partial profiles from about 12%, and no profile from more than half of the samples. In contrast, 85% of the samples from a room where the temperature was 307°C yielded full profiles, 6% partial profiles, and fewer than 10% yielded no profile. An important finding of this work is that at fire scenes, the lack of a positive presumptive test for blood does not preclude the ability to obtain viable DNA evidence.


EXAMPLE PROBLEM 11.3

Calculate the oxygen balance for the following materials: aluminum metal and nitroglycerin (NG, C₃H₅N₃O₉).

Answer:
The first step is to balance the combustion equation, with products going to their completely oxidized state. Any nitrogen is assumed to go to N₂. The relative excess or deficit of oxygen is calculated as a weight percent.
For Al:

\[
\text{Al} + \text{O}_2 \rightarrow \text{Al}_2\text{O}_3
\]

Balanced:

\[
4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3
\]

One way to approach this problem is to use a table, as follows. Note that we do not need to consider the products once the equation is balanced.

<table>
<thead>
<tr>
<th></th>
<th>4Al</th>
<th>3O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Formula weight (g/mol)</td>
<td>27.0</td>
<td>32.0</td>
</tr>
<tr>
<td>Grams</td>
<td>108</td>
<td>96</td>
</tr>
</tbody>
</table>

Oxygen balance:

\[
\frac{96 \text{ g } \text{O}_2}{108 \text{ g } \text{Al}} \times 100 = -89\%
\]

The balance is negative because additional oxygen is required for the reaction to proceed.

For NG:

This part of the problem is more complicated because oxygen is present in the molecule. We need to determine whether the amount is sufficient by itself to support the reaction, so we first balance the equation:

\[
\text{C}_3\text{H}_5\text{N}_3\text{O}_9 \rightarrow 3\text{CO}_2 + \frac{5}{2}\text{H}_2\text{O} + \frac{3}{2}\text{N}_2
\]
\[
2\text{C}_3\text{H}_5\text{N}_3\text{O}_9 \rightarrow 6\text{CO}_2 + 5\text{H}_2\text{O} + 3\text{N}_2
\]
\[
18\text{O} \rightarrow 12 + 5 = 17\text{O}_2; \text{balance for excess}
\]
\[
4\text{C}_3\text{H}_5\text{N}_3\text{O}_9 \rightarrow 12\text{CO}_2 + 10\text{H}_2\text{O} + 6\text{N}_2 + \text{O}_2
\]

Here, oxygen is in excess, so the oxygen balance will be positive.

<table>
<thead>
<tr>
<th></th>
<th>4\text{C}_3\text{H}_5\text{N}_3\text{O}_9</th>
<th>\text{O}_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moles</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Formula weight (g/mol)</td>
<td>227.0</td>
<td>32.0</td>
</tr>
<tr>
<td>Grams</td>
<td>908</td>
<td>32</td>
</tr>
</tbody>
</table>

Oxygen balance:

\[
\frac{32 \text{ g } \text{O}_2}{908 \text{ g } \text{NG}} \times 100 = +3.5\%
\]

### 11.2.2 Kinetics of Combustion

*Kinetics* is the study of the speed of reactions and their mechanisms. Combustion is a complex free-radical process in which many reactions can occur and in which a complex mixture of products forms. The pathways favored and resulting products depend on which reactions are favored under the given conditions.
Combustion does not involve simple single-step collisions between a fuel molecule and an oxidant. Rather, the reactions that occur during combustion are based on free radicals. In a free-radical mechanism, three generic steps take place:

- **initiation**, in which the first free radicals are formed
- **propagation**, in which reactions among radicals produce more radicals
- **termination**, which results from the combination of two free radicals to form a neutral species

Because radicals react with neutrals to create new radicals, a chain reaction results. Each step in a generic free-radical reaction has an associated rate constant. One of these steps will be the slowest and is termed the rate-limiting step. Just as the slowest member of a relay team limits its performance, the rate-limiting step limits the speed of the chemical reaction. The rate-limiting step is generally the step with the highest energy of activation. Partial and simplified steps for the combustion-oxidation of hydrogen are shown in Figure 11.12.

![Sample free-radical reactions that occur in a flame.](image)

**EXHIBIT B**

**It’s a Radical Difference**

Radicals form when a bond such as H—H in H₂ is cleaved homolytically: H₂ → 2H⁺. A heterolytic cleavage would send two electrons to one atom and none to the other: H⁻H → H⁺⁻H⁻⁻. That which causes the formation of the free radical is called the initiator, which may be a chemical species or energy such as UV light. In forensic situations, peroxides (ROOR) are frequently encountered as free-radical initiators: ROOR → 2 RO⁻. The relative stability of radicals is comparable to that of carbocations, with tertiary free radicals being the most stable and primary the least.

The combustion of even a simple hydrocarbon such as methane is extraordinarily complex. A recent count revealed 277 known elementary reactions for this well-studied combustion involving 49 different chemical species.³ Compare this with the combustion of an accelerant such as gasoline, itself a complex mixture of hydrocarbons, and the task of accurately modeling the combustion becomes impossible. Fortunately, in forensic chemical applications, the most important point is that complex and competitive free-radical pathways lead to a mixture of products.

### 11.2.3 Heat Transfer

Heat transfer and heat flow in combustion begins with the premise that all the heat Q evolved in the process goes into heating the products and raising their temperature.† In other words, we assume an adiabatic flame. Excess oxidant (a lean mix) reduces temperature, because Q must be distributed to excess reactant as well as to the products. There are other places heat can and must flow to sustain combustion, some of

---

³Our discussion here will focus on heat transfer via convection (matter transport), but heating by conduction and radiation also take place.
which were seen in Figure 11.4 and which are also shown in simplified form in Figure 11.13. Heated air is less dense than cooler air, and as a result, much of the radiant heat produced in a simple combustion like a burning candle is carried away in rising air and gases. This kind of combustion is also called a **buoyant flame**. Heat is also required for phase transitions, as shown in Figure 11.14. In the candle, the wax must first be melted to liquid and vaporized before combustion occurs. For some heavier hydrocarbons, the melting point and heat needed to vaporize them can be quite high. If $Q$ dwindles, so will the supply of vaporized fuel.

Heat transfer to the substrate has interesting effects on fire behavior and arson investigation. As shown in Figure 11.15 (top frame), heat may reach deep into a substrate such as wood even when oxygen cannot. The result is **pyrolysis** (“fire cutting”) or decomposition in a reducing environment. The products of pyrolysis are different from those of oxidation and can be identified as a layer in burned wood. Typically, the pyrolysis zone is some distance below the burned surface. The layer is defined by the availability of oxygen and by the depth to which heat can penetrate.

The bottom frame of Figure 11.15 illustrates a situation seen in many arson cases: a liquid accelerant such as gasoline is poured over a surface and the vapors are ignited. If the pool is deep enough, it insulates the substrate below and limits the temperature increase. Just as the temperature of liquid water (not steam) cannot exceed 100°C, the temperature of the liquid accelerant cannot exceed its boiling point. Consequently, the pattern of burning and scorching at the edge of the pool and away from it will be different from the patterns directly beneath.

Heat transfer is directly related to the concept of **mass transfer**. $Q$ is used to heat products of the reaction, which, on a molecular level, means that the greater $Q$ is, the more kinetic energy is transferred to the product molecules. This kinetic energy can be transferred to other molecules via collision. However, for that energy to be transferred to key molecules such as those found in the vaporized candle wax, the energy has to be delivered, via fast-moving molecules, to the right place. That movement of mass is called mass transfer.

**FIGURE 11.13** Simplified heat flow paths in a candle flame.

**FIGURE 11.14** Some of the heat generated by the combustion is consumed in the necessary phase transitions of the fuel.
11.2.4 Mass Transfer

Figure 11.4 shows one aspect of mass transfer: the movement of atmospheric O₂ and N₂ to the combustion zone. This diffusion is driven by a concentration gradient, a process aided by rising heated gases. As the heated products rise, surrounding air moves in to fill the void. As these molecules approach the reaction zone, they collide with molecules heated by the combustion, which increases the velocity of those heated molecules. This is a simple view of how heat is conducted in the combustion zone.

Mass transfer and diffusion are also important considerations in evaluating how well the fuel and oxidant mix. In a quiescent (quiet and not mixing) solution of water, a drop of food coloring added will diffuse over time until it is equally distributed throughout the liquid. This is another example of diffusion driven by a concentration gradient. The same will happen in the gas phase. However, in combustion, the process is more complex and dynamic. Consider the simple systems shown in Figure 11.16. Heat transferred to the fuel imparts the energy needed to vaporize the fuel or its pyrolysis products. These vapors diffuse away from the surface, a zone of high concentration. In the combustion zone, the fuel is consumed, as is oxygen, which diffuses inward toward the combustion zone. Figure 11.17 illustrates two simple combustions and the gradients created. The combustion zone approximates the concentration ratios shown in Figure 11.16. The right frame shows a fire burning on a vertical surface such as a wall, and the lower frame shows a “pool fire,” which would occur in an arson in which gasoline was used as an accelerant.
Chapter 11 • The Chemistry of Combustion and Arson 377

**FIGURE 11.16** Concentration gradients of fuel and oxidant as a function of distance. The [] notation refers to concentration.

**FIGURE 11.17** Different views of the concentration gradients and the zones at which the concentrations of the fuel and the oxidant support combustion. Figure 11.8 is superimposed for reference.
Finally, in cases involving a poured liquid accelerant, mass transport of the fuel occurs in a lateral direction, controlled by the characteristics of the surface. Gasoline on a nonporous surface like concrete will diffuse easily, whereas gasoline on a porous surface like wood or carpet will tend to be absorbed. As a result, porous and semiporous surfaces should be sampled in depth, since the chances of finding residual accelerants is increased in such cases.

Applying the Science 11.2 Spontaneous Combustion? Human Candles

One of the more persistent urban myths of forensic science is the belief that the human body can somehow erupt into flame and rapidly burn down to ashes with no discernible ignition source and nearly no peripheral burning. The material discussed in this chapter concerning heat and mass transfer, fuel–air ratios, flammability limits, and the conditions that must be met for successful ignition are sufficient to debunk any ideas of spontaneous human combustion, but the myth persists. To combat misperceptions, a series of experiments was conducted and the results recently reported in the Journal of Forensic Sciences. The author noted that in most cases of spontaneous human combustion, a source of ignition can be located, with cigarettes being one common culprit. The mystery centers on how a body can burn with such ferocity (a large $Q$ value) and become incinerated while nearly all the furniture—even furniture the victim is sitting on—is barely damaged. One theory is the “wick effect,” in which the fat in a body supplies a wick consisting of clothing to facilitate a long burn of a victim such that most of the body’s mass is consumed as fuel, leaving little but small amounts of bone behind. The author of the article cited here conducted experiments and monitored the heat of combustion of biological materials, including fat, tissue, bone, and an amputated leg. The results supported the theory of the wick effect of human combustion, but not spontaneous human combustion.

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11.3 FIRES AND FLAMES

11.3.1 Flames

A common type of fire or flame is a laminar flame, meaning that the flame has definable layers or regions. Within the laminar category, there are two familiar examples: a candle and a Bunsen burner, shown in Figure 11.18. In a Bunsen burner, gaseous methane is mixed with air and injected into the combustion zone. Hot gaseous products diffuse away while atmospheric oxygen diffuses inward, creating a second region in which the fuel–air mixture is no longer in the same proportions as in the premix zone. In a candle, fuel is vaporized and diffuses upward as oxygen diffuses inward. The regions in the candle flame are defined by temperature. Pyrolyzed waxes form particulates (soot) that grow and rise. Partial oxidation occurs, and any residual soot diffuses upward and outward as smoke. In both cases, the flame is self-sustaining once ignited and burns until the fuel is exhausted.

A visible combustion wave is created if the fuel and oxidant gases are stationary, as shown in Figure 11.19. A flame front is visible when, for example, a large puddle of gasoline is ignited at one end and the flames propagate across the surface much as waves on a pond propagate from the point where a stone is dropped into the water. Typical flame velocities for a mixture of methane and air are in the range of approximately 15 to 45 cm/sec, depending on factors such as the fuel–air ratio. In a candle or Bunsen burner, the wave front is stationary because the gases are moving into and out of the combustion zone. The combustion wave remains stationary because the unburned gas molecules are moving away at a rate equal to the burn rate. In simple combustion (deflagration), the combustion wave never exceeds the speed of sound.
As long as the fuel–air mixture remains in the combustible range, the flame will be self-sustaining. The events that bracket the flame “event” are initiation (ignition) and quenching or suppression. The range of combustibility is referred to as the \textit{flammable range} and is defined as the fuel–oxidant ratios that permit steady propagation of the flame. The lower end of the scale is called the \textit{lower flammability limit} (LFL) or the lean limit, whereas the upper range is the \textit{upper flammability limit} (UFL) or rich limit. The terms “lower explosive limit” and “upper explosive limit” (LEL and UEL, respectively) are also used. Some examples are presented in Table 11.2.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11_18.png}
\caption{A Bunsen burner and a candle are examples of \textit{laminar} flames.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11_19.png}
\caption{A visible combustion wave generated in an enclosed tube containing fuel and oxidant.}
\end{figure}
You will note that in Table 11.2, the flammability limits are presented in volume %. How could you use this data to assist in a fire investigation? This information is essential to deciding whether a combustible mixture could have existed in the right place and at the right time to support combustion. For example, assume you are investigating a fire that occurred in a small storage shed with dimensions of 4 ft × 4 ft × 6 ft. Inside the destroyed shed, you find what is left of a propane bottle, labeled as containing 1 lb of propane. Is it possible that the F/A ratio could have supported combustion? Having the dimensions allows you to calculate the total volume of the shed:

\[
4 \text{ ft} \times 4 \text{ ft} \times 6 \text{ ft} = 96 \text{ ft}^3
\]

\[
1 \text{ ft}^3 = 28.32 \text{ L}
\]

\[
96 \text{ ft}^3 \times \frac{28.32 \text{ L}}{1 \text{ ft}^3} = 2718 \text{ L}
\]

Table 11.2 indicates that the flammability range of propane is 2.2%–9.6% by volume. We can use this information and the ideal gas law to estimate what these limits correspond to in liters of propane. Initially, we will assume a temperature of 25°C and a pressure of 1.0 atm:

\[
0.022 \times 2718 \text{ L} = 60 \text{ L}
\]

\[
0.096 \times 2718 \text{ L} = 261 \text{ L}
\]

These values provide an estimate of the volume of fuel that would have to be present. Using the ideal gas law, we can estimate how many moles of propane these volumes correspond to:

\[
\frac{n}{PV} = \frac{RT}{mol \cdot K} = 2.4 \text{ mol at LFL}
\]

\[
\frac{n}{PV} = \frac{RT}{mol \cdot K} = 10.7 \text{ mol at UFL}
\]

The molar mass of propane (C_3H_8) is 44.09 g/mol, and 1.0 lb = 453.59 g, so we can convert the moles to pounds. Of course, you could convert the propane can weight to grams as well; both approaches are valid.

\[
2.4 \text{ mol} \times \frac{44.01 \text{ g}}{\text{ mol}} \times \frac{1.0 \text{ lb}}{453.59 \text{ g}} = 0.2 \text{ lb}
\]

\[
10.7 \text{ mol} \times \frac{44.01 \text{ g}}{\text{ mol}} \times \frac{1.0 \text{ lb}}{453.59 \text{ g}} = 1.0 \text{ lb}
\]
The empty bottle was labeled as containing 1.0 lb of propane, indicating that the contents released into the shed could have supported combustion. You will notice we are being a bit cavalier about significant figures; there is a reason for this. This approach is by its nature an estimate and does not consider many factors that would be important in an arson investigation. For example, we made the implicit assumption that the shed represented a closed system, all the propane left the bottle, and none of the contents escaped the shed. We also estimated temperature and pressure. In this type of situation, all we are after is a reasonable and defensible answer to an investigative forensic question: Could the propane have supported combustion? In this case, there was sufficient propane to sustain combustion. However, this would represent a starting point for further investigation, not the end. Alone, this calculation would not prove or disprove arson, but it would provide investigators with important information.

As demonstrated and discussed already, many other variables will alter the fuel/air ratio that exists in a given place at a given time. Because the fuel and oxidant are gases, pressure and temperature are among the most important variables to be considered in a fire investigation. For example, the higher the temperature, the wider is the flammable range. In arson cases, homogeneous mixtures rarely exist, and the relative densities of materials become critical factors, as shown in Figure 11.20.

The weighted-average formula weight of air is taken to be approximately 29 g/mol. The relative weight of hydrogen (H\textsubscript{2}; formula weight FW ~ 2) is therefore 2/29, or about 0.07. If hydrogen is released into the air, it rapidly dissipates upward and away from the release point. Conversely, gasoline vapors tend to sink. If gasoline is crudely represented by \textit{n}-octane (C\textsubscript{8}H\textsubscript{18}; FW ~ 114), the weight ratio relative to air is 114/29, or ~3.9. Therefore, in a quiescent or nearly quiescent environment, fuel vapors disperse according to their weight and density. This phenomenon is illustrated in Figure 11.20.

The presence of vapors within the explosive limits is a necessary condition for combustion to occur, but it is not a sufficient one. The initial \(E_a\) barrier must be overcome, and the energy to do so is supplied by an ignition source that must have sufficient energy available and that must remain in contact with the flammable mixture long enough to ignite it. In arson investigations, the ignition source is called an \textit{incendiary device}, such as a match, a cigarette, or a more sophisticated apparatus. As demonstrated in Figure 11.20, this device must also be in the right place at the right time. In that example, gasoline has been poured down the basement stairs and enough time has passed that a stratification has developed in this closed, quiescent system. The gasoline vapors, which are heavier than air, move lower in the room and create a rich layer near the floor. Someone wanting to ignite the mixture would have to place the incendiary device in the flammable region. A match tossed to the floor would not work because the mixture is too rich, and a spark at the top of the stairs would fail because there the mixture is too lean. In addition, the incendiary device would have to produce sufficient energy to initiate the

![Figure 11.20](image-url)
reaction and would have to be in contact with the reaction mixture long enough to ensure the combustion had become self-sustaining. The energy needed to ignite a mixture is usually thermal. Kinetic energy is transferred to the reactants via collisions among the molecules of the mixture. The collisions may be instantaneous, as in the case of someone using a striker and spark to ignite a Bunsen burner, but even the biggest spark will not ignite a mixture that will not support combustion. In other cases, ignition takes much more time, as when a smoldering cigarette is placed between the cushions of a couch. With explosives, pressure can provide sufficient energy for combustion.

11.3.2 Fire Dynamics

A fire is a time-dependent event that has definable phases and dynamics. After ignition, a fire will grow until it reaches a steady state that depends on the amounts of fuel and oxidant available in the given environment. In the steady state, the fire triangle requirements of fuel–oxidant–heat are met, and the fire burns steadily. As one or more of the key ingredients dissipates, the fire begins to decay and is eventually quenched, although destruction and residual heat linger after the flame itself goes out. Of course, the behavior of any given fire will be more complex even while it follows this general model. How a fire behaves during its lifetime has important consequences for the fire investigator and the forensic chemist. The dynamics of a fire will depend on all the factors described so far, which combine to make each fire event unique, although some generalizations can be made.

In an arson fire, there are one or more points of origin for the fire, and an understanding of fire dynamics is essential to locating these points. As noted earlier, conventional fires are diffusion types in which heated gases move upward and outward from the combustion zone. Such flames are also referred to as buoyant flames, since the heated gases are less dense, and thus more buoyant, than the unheated gases. Consequently, flames burn in plumes that can leave distinctive physical and chemical evidence. A simple buoyant flame is shown in the top frame of Figure 11.21. Since the hot gases are moving upward and outward, a V-shaped burn pattern on adjacent surfaces is often observed. Given that a fire usually burns the longest at the point of origin, the V pattern often marks this spot. If the fire burns in an enclosed room, a ceiling jet will form in which the hot gases and smoke are forced outward.

If the fire is sufficiently intense, flashover may occur. In a fire in an enclosed room, for example, flashover is the point at which all the flammable vapors in the room ignite. A fire started in a corner can generate enough heat and vapors from furniture, paint, and flooring that the entire room erupts in flame, and what was a fire burning in one or more isolated locations becomes generalized. Flames extend out through openings, and windows can be broken out by the sudden creation of hot gaseous combustion products. If the room is tightly enclosed, flames may subside to a smoldering state that can erupt again if a door or window is suddenly opened, allowing oxygen in. A similar situation can result if a fire only smolders in an enclosed space, depleting oxygen over time without the telltale flames. A door opened in this situation can cause immediate flashover in a room rich in fuel vapors. Flashover is a significant danger to firefighters and first responders to fire scenes.

11.4 ARSON AND FIRE INVESTIGATION

During the years 2003–2007, more than 53,000 intentionally set fires were reported in the United States, causing 387 deaths, and more than $900 million in property damage. Half of these were set in homes, and 8% of residential fires were intentionally set.5
Intentionally set fires, or arson, usually involve an accelerant of some type, as well as an incendiary device used to ignite it, and these two components create the physical evidence forensic chemists work with. Arson fires are also referred to as incendiary fires. For fires set in homes, a bedroom was the most common point of origin; fires set in public buildings were usually started in bathrooms. From a law enforcement point of view, arson is a difficult crime to clear; in 2008, only 18% of arson cases were cleared by arrest or other means. Nearly half of those arrested were under 18, and 3% were under 10 years of age.5,6

One of the challenges of fire investigation is the classification of a fire as natural, accidental, or incendiary (arson). Fire investigators utilize evidence at the scene, as well as forensic analysis, to make such determinations. One of the most important pieces of information required in making a determination of arson is the location of the point or points of origin of the fire. Multiple points of origin are strongly indicative of an intentionally set fire, whereas a point of origin at an electrical outlet suggests an accidental fire. As discussed in Section 11.3, the behavior of a fire creates predictable damage that is useful in locating a point of origin. Although such fire and fire scene investigations are critical in determinations of arson, we will focus on the chemical analysis aspects of fire and arson investigation. The former is fire investigation; the latter is forensic chemistry.

11.4.1 Accelerants and Incendiary Devices

An accelerant is anything that is intentionally placed at a scene to start and sustain a fire. Accelerants can be solids (wood, paper, road flares), liquids (gasoline), or gases (natural gas, propane). Although a gaseous accelerant will not leave chemical residues, there will always be physical evidence related to the container used to hold or deliver it. For example, if bottled propane is used to start a fire, the bottle will remain even though the propane will not. As with any type of combustion, fuel, oxidant, and a source of ignition are required, and the forensic chemist will be concerned with two of these three: the fuel, such as an accelerant, and the incendiary device. The latter can be as simple as a match, a candle, or a smoldering cigarette. More complex devices are also seen; however, we will focus on the analysis of accelerants, since they represent the bulk of the casework seen by forensic chemists. The most common accelerants are liquid petroleum distillate products. Also frequently seen as physical evidence are gasoline, kerosene, and diesel fuel.

As the name implies, petroleum distillates are extracted from crude oil by distillation. The process shown in Figure 11.22 is one of many available, but for our purposes, it is the most useful because of the parallels between distillation and gas chromatography.7 As shown in the figure, crude oil is introduced into the cracking tower and heated to about 350°C, volatilizing much of its content. The vapors rise, cool, and condense, whereupon they are collected on plates and removed. The heavier fractions, such as diesel and kerosene, are collected lower in the tower than are gasolines and fuel gases. The separation is not complete, and each fraction collected consists of a mixture of hydrocarbon components with similar boiling points. This separation is re-created on a small scale when samples are analyzed by gas chromatography, which separates components on the basis of their volatility and preferential partitioning on a solid phase.

---

5 Recall that one measure of the efficiency of a chromatographic column is the number of theoretical plates. This analogy is drawn from distillation: the more collection plates in the column, the more effective is the separation. The maximum number of plates (N) is achieved when the distance between them (i.e., the smallest possible height of a plate, HETP) is minimized.
11.4.2 Forensic Analysis of Fire Debris

The most frequently encountered accelerants are readily available petroleum distillates such as gasoline, jet fuel, and kerosene. ASTM has published a classification for ignitable liquids that is widely used as part of the forensic analysis of fire debris; a summary is presented in Table 11.3. Each class is further subdivided into three groups based on carbon chain length, which correlates with volatility. As we will see shortly, volatility plays an important role in laboratory analysis.

Fire debris evidence is collected in coated paint cans of various sizes with a predrilled hole sealed with a septum. The debris is placed loosely in the can, leaving plenty of headspace above. As with all paint cans, the can is closed by pounding the lid into the metal lip. This creates an airtight seal that traps vapors, including any residual volatile accelerants. Table 11.4 and Figure 11.23 summarize existing ASTM-recommended protocols for fire debris preparation and analysis. They also summarize the evolution of sample preparation methods over the past decades. The first protocols involved steam distillation. Fire debris (slightly wet) is transferred to a distillation apparatus, and heat is applied. As the vapors rise in the distillation column they are cooled and condense, dropping into a collection thimble. Any petroleum products collect as a layer atop water. This approach is effective in separating and concentrating accelerants but is time consuming and relatively aggressive, meaning that more volatile components can be lost.

The next development in sample preparation was solvent extraction of fire debris with pentane and carbon disulfide (CS$_2$). Solvent is added to the evidence, collected, and concentrated into a small volume (about 1–5 mL). Both pentane and (CS$_2$) are nonpolar and well suited to solvation of petroleum hydrocarbons, but both also have limitations. Pentane is extremely volatile, so care must be taken to ensure that the solvent extract does not go to dryness. If it does, the lighter fractions will be lost along with the pentane. Carbon disulfide is not as volatile, but it is relatively toxic and has a foul odor. Additionally, solvent extraction, like steam distillation, is relatively aggressive and can result in a loss of the more volatile fractions of residual accelerants.

Currently, the favored methods of sample preparation are based on headspace (Chapter 5, section 5.2 and Chapter 10, 10.3.3). The headspace may be heated or unheated, passive or active. All headspace methods involve concentrating volatiles into a solid phase by adsorption. The effect is the same as a solvent extraction: target analytes are extracted from the fire debris matrix and concentrated on the adsorbent. Generically, this protocol is called trapping, and in the case of fire debris, the trap is made of charcoal. In simple passive methods, a polymer strip coated with charcoal is dangled above the fire debris, and the evidence can be resealed. Gentle heating drives the volatiles into the vapor phase, from which they move via diffusion to the charcoal, where they are adsorbed. At the end of the heating time, the charcoal strip is removed.
and extracted with a solvent such as CS₂. Active or dynamic headspace (DHS), also called *purge-and-trap*, is a methodology widely used in environmental analysis. In DHS, an inert gas constantly flows through the heated container, carrying volatiles downstream to a trap. Because the equilibrium is constantly disturbed by removal of

### TABLE 11.3 Classification of Ignitable Liquids (after ASTM)

<table>
<thead>
<tr>
<th>Class</th>
<th>Light (C₄–C₉)</th>
<th>Medium (C₁₀–C₁₃)</th>
<th>Heavy (C₈+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>Primarily C₄–C₁₂</td>
<td></td>
<td>Kerosene, diesel oil</td>
</tr>
<tr>
<td>Petroleum distillates</td>
<td>Pet ether Lighter fluids (butane)</td>
<td>Charcoal starter fluids</td>
<td>Specialty solvents</td>
</tr>
<tr>
<td>Isoparaffinics</td>
<td>Aviation gas (av gas)</td>
<td>Paint thinners, copier toners</td>
<td>Specialty solvents</td>
</tr>
<tr>
<td>Aromatics</td>
<td>Toluene and xylene, degreasers</td>
<td>Degreasers, specialty cleaning agents, fuel additives</td>
<td>Industrial cleaning solvents</td>
</tr>
<tr>
<td>Naphthenic paraffins</td>
<td>Cyclohexane-based solvents</td>
<td>Lamp oils</td>
<td>Lamp oils, industrial solvents</td>
</tr>
<tr>
<td>n-Alkanes</td>
<td>Solvents to heptane</td>
<td>Candle oils</td>
<td>Copier toners</td>
</tr>
<tr>
<td>De-aromatized distillates</td>
<td>Camp stove fuels</td>
<td>Some paint thinners</td>
<td>Odorless kerosenes</td>
</tr>
<tr>
<td>Oxygenated solvents</td>
<td>Ketones, lacquers</td>
<td>Metal cleaners</td>
<td></td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>Blends</td>
<td>Turpentines</td>
<td>Specialty products</td>
</tr>
</tbody>
</table>


### TABLE 11.4 ASTM Standards Relevant to Fire Debris Analysis

<table>
<thead>
<tr>
<th>Number (E-)</th>
<th>Title and Subject</th>
</tr>
</thead>
<tbody>
<tr>
<td>1385</td>
<td>Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Steam Distillation</td>
</tr>
<tr>
<td>1386</td>
<td>Practice for the Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction</td>
</tr>
<tr>
<td>1387</td>
<td>Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography</td>
</tr>
<tr>
<td>1388</td>
<td>Practices for Sampling of Headspace Vapors from Fire Debris Samples</td>
</tr>
<tr>
<td>1389</td>
<td>Cleanup of Fire Debris Samples Extracts by Acid Stripping³</td>
</tr>
<tr>
<td>1412</td>
<td>Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Activated Charcoal</td>
</tr>
<tr>
<td>1413</td>
<td>Practice for Separation and Concentration for Ignitable Liquid Residues for Fire Debris Samples by Dynamic Headspace Concentration</td>
</tr>
<tr>
<td>1618</td>
<td>Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography Mass Spectrometry</td>
</tr>
<tr>
<td>2154</td>
<td>Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Solid Phase Microextraction</td>
</tr>
</tbody>
</table>

³Used to remove nitrogenous and oxygenated species from a prepared extract.
FIGURE 11.23 Depiction of the sample preparations used in analyzing fire debris.

FIGURE 11.24 The types of containers used to collect fire debris samples.
product, the volatiles are efficiently extracted and trapped. Solvents are used to desorb
the sample traps. DHS methods are particularly effective with low concentrations of
residual accelerants.

\[ \text{analytes (debris)} \rightleftharpoons \text{analytes (vapor)} \]

Another passive method of vapor preconcentration is solid phase microextraction (SPME). The procedure is much like that used for the charcoal strip, except that
other adsorbents are used to coat the silica needle. The needle can be directly intro-
duced into the gas chromatograph for thermal desorption, or a solvent extraction can be
employed. An added advantage of SPME is versatility: The fiber can be immersed in
an aqueous matrix if the fire debris is waterlogged. Currently, ASTM lists as a screening
technique standard E 2154-01, but high sensitivity and a solventless approach make the
SPME method increasingly attractive. A chromatogram of the same sample prepared
by different methods is presented in Figure 11.25. Note the peak to the far left on the
lower two frames, attributable to the solvent used in the extraction. Detection was with
a flame ionization detector (FID), and the sample was gasoline on charred carpet.

No matter what sample preparation method is used, discrimination occurs, and
there are inherent limitations. Analyses of fire debris samples are designed to detect a
wide range of compounds and, as a result, are not optimized for any one compound.
Headspace methods will be biased toward the more volatile materials, even under con-
ditions of gentle heating. Excessively aggressive heating can drive off the more vol-
atile fractions, so heating temperature is limited and typically falls into the range of
approximately 70°C. The efficiency of a solvent extraction, like any other partitioning,
will depend on the relative polarities of the solutes and solvent; in a complex hydrocar-
bon mixture, discrimination is inevitable, and some compounds will be desorbed more
efficiently than others. Similarly, not all components of an accelerator will be adsorbed
with equal efficiency onto charcoal or other solid phases. These caveats do not mean
that the methods are fatally flawed, but they do mean that the limitations of each tech-
nique must be understood and that validated methods are essential. In the case of fire
debris, the conditions that are optimal for the collection of gasoline components are
likely not optimal for heavy distillates, and vice versa; the discrepancy is even more
critical when nonpetroleum products, such as methyl ethyl ketones or industrial clean-
ing solvents, are involved. However, keep in mind that the transfer (from debris to in-
strument) does not have to be 100% efficient for every compound that might be in the
matrix. Rather, the transfer of each target compound must be in an acceptable range and
also must be reproducible. The analysis of fire debris is qualitative, not quantitative,
and is based on pattern matching, not the presence or absence of any one component.
As we will see, pattern matching is widely used in materials analysis as well.

Regardless of the type of sample preparation, the instrumental method employed
for fire debris analysis is gas chromatography, coupled to either a flame ionization de-
tector or a mass spectrometer. Unlike other chromatographic methods used in forensic
chemistry, the primary goal (in most cases) is to recognize patterns rather than identify
specific compounds. The pattern of gasoline (Figure 11.25) differs significantly from the
pattern of diesel fuel (Figure 11.26, bottom frame), which is composed of heavier and less
volatile hydrocarbons. With the use of mass spectrometry, the patterns can be further
analyzed to identify significant groups of compounds within a sample, such as aromat-
ics, alkanes, and branched alkanes. In addition to recognizing patterns and groups
of compounds, the analyst must consider environmental factors. Accelerants undergo
weathering, and their composition changes over time. The changes are predictable in
that the more volatile a compound is, the more quickly it will be lost. For gasolines, then,
weathering is more of an issue than it is for diesel fuel. Understanding weathering and
the analysis of weathered samples is essential to interpreting analytical results.
Also essential in any fire debris analysis is the collection and analysis of background samples (matrix controls). For example, if debris suspected of containing an accelerant is collected on a carpet, samples of undamaged carpet should be collected as well, if at all possible. Carpeting is manufactured from synthetic fibers (Chapter 16), the raw materials of which are polymers, many derived from petroleum products. As seen in Figure 11.26, many common materials produce patterns that could be confused with accelerants. The data shown in this figure were collected by means of passive headspace–charcoal strips and heating at 80°C for 16 hours. The instrument used was a GC-MS, but the patterns of the total ion chromatogram (TIC) are comparable to patterns that would be obtained from a GC-FID. The figure illustrates the vital nature of controls in fire debris analysis.

**EXAMPLE PROBLEM 11.4**

An officer submitting fire debris requests that you analyze it for the presence of gasoline with ethanol. Would you use GC-FID or GC-MS?

**Answer:**

GC-MS. The FID detector would respond to ethanol (it is widely used for blood alcohol analysis), but the response is not specific. Because a complex pattern of peaks would be expected from such a sample, it would be difficult to definitively identify one as ethanol, although it would likely be one of the earliest eluting peaks. A mass spectrometer could provide definitive identification of ethanol via the compound’s mass spectrum coupled with retention time data and comparison to reference ethanol standards.
Whereas identifying residual accelerants is a well-developed forensic protocol, classifying an accelerant beyond gasoline, diesel fuel, and the like is a difficult or impossible task. Part of the difficulty is attributable to weathering and environmental factors, part to the mass-production nature of distillates such as gasoline. Attempts have been made to allow for greater discrimination by targeting compounds other than hydrocarbons, such as oxygenates. Ethanol is added to many gasoline formulations on a seasonal basis, so identifying ethanol in a solvent mixture could provide valuable investigatory information. Oxygenates are added to gasoline for similar reasons, to increase the oxygen balance and improve the efficiency of combustion. Ethanol is a common oxygenate in gasoline and is suitably volatile for headspace detection methods.

**Summary**

From flame to bomb, the underlying chemistry of combustion is the same: a rapid oxidative decomposition that produces large volumes of hot expanding gases. A slower reaction front produces deflagration, whereas a rapid and confined mixture can detonate. In this chapter, we discussed combustion chemistry generically and then focused on how these principles apply to intentionally set fires in arson. We also discussed how forensic analytical chemistry approaches arson investigations, taking advantage of the volatile nature of many accelerants. In the next chapter, we will move into the chemistry and evidence associated with firearms.

**Key Terms and Concepts**

<table>
<thead>
<tr>
<th>Term</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerant</td>
<td>378</td>
</tr>
<tr>
<td>Adiabatic combustion</td>
<td>367</td>
</tr>
<tr>
<td>Buoyant flame</td>
<td>375</td>
</tr>
<tr>
<td>Cracking</td>
<td>383</td>
</tr>
<tr>
<td>Deflagration</td>
<td>360</td>
</tr>
<tr>
<td>Detonation</td>
<td>360</td>
</tr>
<tr>
<td>Fuel/air ratio (F/A)</td>
<td>369</td>
</tr>
<tr>
<td>Incendiary device</td>
<td>381</td>
</tr>
<tr>
<td>Laminar flame</td>
<td>378</td>
</tr>
<tr>
<td>Lean mixture</td>
<td>369</td>
</tr>
<tr>
<td>Lower flammability limit</td>
<td>379</td>
</tr>
<tr>
<td>(LFL)</td>
<td></td>
</tr>
<tr>
<td>Mass transfer</td>
<td>375</td>
</tr>
<tr>
<td>Matrix controls</td>
<td>388</td>
</tr>
<tr>
<td>Oxygen balance</td>
<td>371</td>
</tr>
<tr>
<td>Petroleum distillate</td>
<td>383</td>
</tr>
<tr>
<td>Points of origin</td>
<td>382</td>
</tr>
<tr>
<td>Propellants</td>
<td>360</td>
</tr>
<tr>
<td>Pyrolysis (combustion reactions)</td>
<td>375</td>
</tr>
<tr>
<td>Rich mixture</td>
<td>369</td>
</tr>
<tr>
<td>Saltpeter</td>
<td>360</td>
</tr>
<tr>
<td>Stoichiometric equivalence</td>
<td></td>
</tr>
<tr>
<td>(STE)</td>
<td>368</td>
</tr>
<tr>
<td>Upper flammability limit</td>
<td></td>
</tr>
<tr>
<td>(UFL)</td>
<td>379</td>
</tr>
<tr>
<td>Weathering</td>
<td>387</td>
</tr>
</tbody>
</table>

**Problems**

**FROM THE CHAPTER**

1. Suppose that 1.00 gram of nitroglycerin is used in a firearm as a propellant. Suppose also that combustion is 100% efficient and that 65% of the chemical energy is transferred to a bullet that weighs 115 grains. How fast will the bullet be moving? Will it exceed the speed of sound?
2. How is a shotgun like a pipe bomb in terms of energy conversion? How is it different?
3. ANFO is a powerful explosive mixture containing ammonium nitrate and fuel oil. It was used in the 1995 bombing of the Alfred P. Murrah Federal Building in Oklahoma City. Optimal power, related to $Q$, is obtained with a mixture of about 94% $\text{NH}_4\text{NO}_3$ and 6% fuel oil. What is the approximate oxygen balance of fuel oil? Three compounds that have been used as fuel in cars and racing cars are ethanol, nitromethane ($\text{CH}_3\text{NO}_2$), and gasoline. Using octane as representative of gasoline, calculate the following quantities for each compound: $\Delta H^\circ$ of combustion per mole of the fuel, moles of gas produced per mole of fuel at 25°C and 1 atm pressure, $Q$ produced per gram of fuel, liters of gas produced per gram of fuel at 25°C and 1 atm, and the QV value. Assume that all components are in the gas phase. Which fuel would be the best choice based on these considerations? You may need to look up some heat of formation values.

4.
5. Through a balanced equation of combustion, calculate the oxygen balance of the following compounds. Assume that the combustion is complete and produces fully oxygenated species.
   a) Ammonium nitrate
   b) HMX (Octogen)
   c) Picric acid
6. The propellant used in the solid rocket boosters during the space shuttle program was based on aluminum metal and ammonium perchlorate. If these were the only two ingredients, what composition would produce a net zero oxygen balance?
7. Assume that the two main ingredients in a gunpowder formulation are nitrocellulose (NC) and nitroglycerin (NG). If these were the only active ingredients, what composition would produce a net zero oxygen balance? Assume that the oxygen balance of NC is \(-24\%\).
8. According to the UFL and LFL for flammables listed in Table 11.2, which would be “better” choices for setting an arson fire based strictly on these criteria? Why?
9. You are called to a fire scene in which the point of origin appears to be in a restroom in a high school. The dimensions of the room are 25 ft x 10 ft x 10 ft. In one corner, you find the burned remains of a small tank labeled acetylene that appears to have been stolen from the high school welding shop. You call the supplier and learn that a full tank contains 25 lb of acetylene. The shop teacher says the tank was new and barely used. Estimate the LFL and UFL in pounds and determine if a combustible mixture would be supported. Assume 1.0 atm pressure and a typical indoor temperature of 25°C.
10. Is SPME a destructive analysis? Justify your answer.
11. Two common solvents used in clandestine drug laboratories are diethyl ether and acetone. Being less than vigilant in laboratory and safety practices, clandestine chemists often work with leaky equipment. If a person was brought to an emergency room under suspicious circumstances, where would you predict the burn patterns on the person’s body to be most pronounced if he or she was injured by a fire or explosion at a clandestine laboratory?

**FOOD FOR THOUGHT**

1. Hydrogen is billed as “the fuel of the future” for automobiles. A popular misconception, mostly owing to films of the Hindenburg disaster, is that cars that store hydrogen as fuel will be more likely to explode in an accident than current cars that use gasoline. Why is this a misconception?

**Further Reading**


**References**

Part IV • Combustion Evidence


