Thermochemistry

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Introduction

Thermochemistry is the branch of physical chemistry that is concerned with the amounts of energy released or absorbed when a chemical change (reaction) takes place [1–3]. Inasmuch as fire is fundamentally a manifestation of a particular type of chemical reaction, viz., combustion, thermochemistry provides methods by which the energy released during fire processes can be calculated from data available in the scientific and technical literature.

To place it in context, thermochemistry is a major derivative of the first law of thermodynamics, which is a statement of the principle of conservation of energy. However, while concerned with chemical change, thermodynamics does not indicate anything about the rate at which such a change takes place or about the mechanism of conversion; this falls within the topic of chemical kinetics [4]. Consequently, the information it provides is normally used in association with other data, for example, to enable the rate of heat release to be calculated from the rate of burning.

The First Law of Thermodynamics

It is convenient to limit the present discussion to chemical and physical changes involving gases; this is not unreasonable, as flaming combustion takes place in the gas phase. It may also be assumed that the ideal gas law applies, that is,

$$PV = n \cdot RT \tag{5.1}$$

where P and V are the pressure and volume of n moles of gas at a temperature, T (in degrees Kelvin); values of the universal gas constant (R) in various sets of units are summarized in Table 5.1. At ambient temperatures, deviations from "ideal behavior" can be detected with most gases and vapors, while at elevated temperatures such deviations become less significant. In this context, it should be noted that whereas the terms *gas* and *vapor* are sometimes used interchangeably, it is best to make a distinction. Both are in the gaseous state, but as a general rule a vapor at normal temperatures can be made to liquefy if the pressure of the vapor is increased sufficiently. Thus, propane can be stored as a liquid under a relatively low pressure (approximately 8.4 bar at 293 Kelvin) whereas the permanent gases (particularly hydrogen, helium, oxygen, and nitrogen) can only be stored as gases at ambient temperatures, typically in pressure cylinders at 2000 psi (c. 138 bar). Again, as a general rule, vapors tend to deviate more strongly from ideal gas behavior than do the permanent gases.

Internal Energy

As a statement of the principle of conservation of energy, the first law of thermodynamics deals

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Table 5.1 Values of the ideal gas constant, R

Units of pressure	Units of volume	Units of R	Value of R
Pa (N/m^2)	m^3	J/K·mol	8.31431
atm	cm^3	cm^3·atm/K·mol	82.0575
atm	*l*	*l*·atm/K·mol	0.0820575
atm	m^3	m^3·atm/K·mol	8.20575×10^{-5}

with the relationship between work and heat. Confining our attention to a "closed system"—for which there is no exchange of matter with the surroundings—it is known that there will be a change if heat is added or taken away, or if work is done on or by "the system" (e.g., by compression). This change is usually accompanied by an increase or decrease in temperature and can be quantified if we first define a function of state known as the internal energy of the system, E. Any change in the internal energy of the system (ΔE) is then given by

$$\Delta E = q - w \tag{5.2}$$

where q is the heat transferred to the system, and w is the work done by the system. This can be expressed in differential form

$$dE = dq - dw \tag{5.3}$$

Being a function of state, E varies with temperature and pressure, that is, $E = E(T, P)$.

According to the standard definition, work, w, is done when a force, F, moves its point of application through a distance, x, thus, in the limit

$$dw = F \cdot dx \tag{5.4}$$

The work done during the expansion of a gas can be derived by considering a cylinder/piston assembly (Fig. 5.1); thus

$$dw = P \cdot A \cdot dx = P\,dV \tag{5.5}$$

where

P = Pressure of the gas

A = Area of the piston

dx = Distance through which the piston is moved; the increment in volume is therefore $dV = A \cdot dx$

The total work done is obtained by integrating Equation 5.5 from the initial to the final state; that is,

$$w = \int_{\text{initial}}^{\text{final}} P \cdot dV \tag{5.6}$$

Combining Equations 5.3 and 5.5, the differential change in internal energy can be written

$$dE = dq - P \cdot dV \tag{5.7}$$

This shows that if the volume remains constant, as $P \cdot dV = 0$, then $dE = dq$; if this is integrated, we obtain

$$\Delta E = q_v \tag{5.8}$$

where q_v is the heat transferred to the constant volume system; that is, the change in internal energy is equal to the heat absorbed (or lost) at constant volume.

Enthalpy

With the exception of explosions in closed vessels, fires occur under conditions of constant pressure. Consequently, the work done as a result of expansion of the fire gases must be taken into account. At constant pressure, Equation 5.5 may be integrated to give

$$w = P \cdot (V_2 - V_1) \tag{5.9}$$

where V_1 and V_2 are the initial and final volumes, respectively. Equation 5.2 then becomes

$$\Delta E = E_2 - E_1 = q_p + PV_1 - PV_2 \tag{5.10}$$

or, rearranging,

$$\begin{aligned} q_p &= (E_2 + PV_2) - (E_1 + PV_1) \\ &= H_2 - H_1 \end{aligned} \tag{5.11}$$

where q_p is the heat transferred at constant pressure, and H is known as the enthalpy ($H \equiv E + PV$). The change in enthalpy is therefore the heat

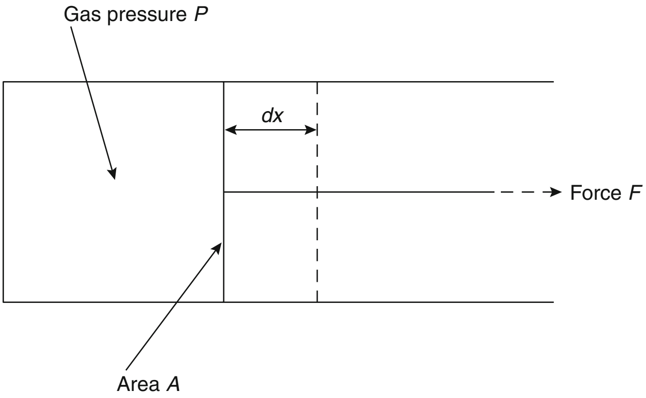

Fig. 5.1 Cylinder/piston assembly

absorbed (or lost) at constant pressure (provided that only $P - V$ work is done), and consequently it is the change in enthalpy that must be considered in fire-related problems.

Specific Heat

Specific heat, or heat capacity, of a body or "system" is defined as the amount of heat required to raise the temperature of unit mass by 1°C; the units are J/kg K, although for most thermochemical problems the units J/mol K are more convenient. The formal definition of the "mole" is the amount of a substance (solid, liquid, or gas) that contains as many elementary units (atoms or molecules) as there are carbon atoms in exactly 0.012 kg of carbon-12 (C^{12}). This number—known as Avogadro's number—is actually 6.023×10^{23}; in its original form, Avogadro's hypothesis was applied to gases and stated that equal numbers of molecules of different gases at the same temperature and pressure occupy the same volume. Thus, the quantity of a substance that corresponds to a mole is simply the gram-molecular weight, but expressed in kilograms to conform with SI units. For example, the following quantities of the gases N_2, O_2, CO_2, and CO represent 1 mole of the respective gas and, according to Avogadro's hypothesis, will each occupy 0.022414 m^3 at 273 K and 760 mmHg (101.1 kPa):

0.028 kg nitrogen (N_2)
0.032 kg oxygen (O_2)
0.044 kg carbon dioxide (CO_2)
0.028 kg carbon monoxide (CO)
0.016 kg methane (CH_4)
0.044 kg propane (C_3H_8)

The concept of specific heat is normally associated with solids and liquids, but it is equally applicable to gases. Such specific heats are required for calculating flame temperatures, as described below. Values for a number of important gases at constant pressure and a range of temperatures are given in Table 5.2.

It is important to note that there are two distinct heat capacities; at constant pressure, C_p, and at constant volume, C_v. Thus, at constant pressure

$$dq_p = dH = C_p \cdot dT \tag{5.12}$$

while at constant volume

$$dq_v = dE = C_v \cdot dT \tag{5.13}$$

For an ideal gas, $C_p = C_v + \mathrm{R}$.

Heats of Combustion

Chemical Reactions and Stoichiometry

When chemical reactions occur, they are normally accompanied by the release or absorption of heat. Thermochemistry deals with the

Table 5.2 Heat capacities of selected gases at constant pressure (101.1 kN/m^2) [5]

Cp (J/mol K)					
Temperature (K)	298	500	1000	1500	2000
Species					
CO	29.14	29.79	33.18	35.22	36.25
CO_2	37.129	44.626	54.308	58.379	60.350
H_2O(g)	33.577	35.208	41.217	46.999	51.103
N_2	29.125	29.577	32.698	34.852	35.987
O_2	29.372	31.091	34.878	36.560	37.777
He	20.786	20.786	20.786	20.786	20.786
CH_4	35.639	46.342	71.797	86.559	94.399

quantification of the associated energy changes. This requires a definition of the initial and final states, normally expressed in terms of an appropriate chemical equation, for example,

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad (5.R1)$$

in which the reactants (propane and oxygen) and products (carbon dioxide and water) are specified. This balanced chemical equation defines the *stoichiometry* of the reaction, that is, the exact proportions of the two reactants (propane and oxygen) for complete conversion to products (no reactants remaining). Note that the physical states of the reactants and products should also be specified. In most cases, the initial conditions correspond to ambient (i.e., 25 °C and atmospheric pressure) so that there should be no doubt about the state of the reactants. In this case both are gaseous, but it is more common in fires for the "fuel" to be in a condensed state, either liquid or solid. As an example, the oxidation of *n*-hexane can be written

$$C_6H_{14} + 9.5O_2 \rightarrow 6CO_2 + 7H_2O \qquad (5.R2)$$

but the fuel may be in either the liquid or the vapor state. The consequences of this will be discussed below.

Reaction 5.R1 may be used to calculate the mass of oxygen or air required for the complete oxidation of a given mass of propane. Thus, we deduce that 1 mole of propane (44 g) reacts completely with 5 moles of oxygen ($5 \times 32 = 160$ g); that is, 1 g propane requires 3.64 g oxygen. If the propane is burning in air, then the presence of nitrogen needs to be taken into account, although it does not participate to any significant extent in the chemical change. As the ratio of oxygen to nitrogen in air is approximately 21:79 (or 1:3.76), Reaction 5.R1 can be rewritten

$$C_3H_8 + 5O_2 + 18.8N_2 \rightarrow 3CO_2 + 4H_2O + 18.8N_2 \qquad (5.R3)$$

(where $18.8 = 5 \times 3.76$), showing that 44 g propane requires ($160 + 18.8 \times 28$), or 686.4 g of "air" for complete combustion, that is, 15.6 g air/g propane. Calculations of this type are valuable in assessing the air requirements of fires.

Thus, on the assumption that wood has the empirical formula [5] $CH_{1.5}O_{0.75}$, it can be shown that its stoichiometric air requirement is 5.38 g air for each gram of fuel, assuming complete combustion of wood to CO_2 and H_2O. The relevant stoichiometric equation is

$$\begin{aligned} &CH_{1.5}O_{0.75} + O_2 + 3.76N_2 \\ &\quad = CO_2 + 0.75H_2O + 3.76N_2 \end{aligned} \qquad (5.R4)$$

In this calculation no distinction is made of the fact that flaming combustion of wood involves oxidation of the volatile gases and vapors produced by the pyrolysis of wood, while the residual char burns much more slowly by surface oxidation.

Measurement of Heats of Combustion

The heat of combustion of a fuel is defined as the amount of heat released when unit quantity is oxidized completely to yield stable end products.

In the present context, the relevant combustion processes occur at constant pressure so that we are concerned with an enthalpy change, ΔH_c. By convention, for exothermic reactions such as oxidation, values of ΔH_c are negative; that is, the reaction produces energy that can then be lost from the system. (By contrast, an endothermic reaction such as the conversion of water to hydrogen and oxygen will take place only if energy is provided in a suitable form.)

Heats of combustion are measured in the combustion bomb calorimeter in which a precise amount of fuel is burned in pure oxygen inside a pressure vessel whose temperature is strictly monitored. The apparatus is designed to reduce heat losses from the calorimeter to a minimum so that the amount of heat released can be calculated from the rise in temperature and the total thermal capacity of the system; corrections can be made for any heat loss. In the past, combustion bomb calorimetry received a great deal of attention within physical chemistry [1, 6] as the technique was able to provide a wealth of data of relevance to thermochemistry. However, the experiment gives the heat released at constant volume; that is, the change in internal energy, ΔE (Equation 5.8). The change in enthalpy is given by

$$\Delta H = \Delta E + \Delta(PV) \tag{5.14}$$

where $\Delta(PV)$ is calculated using the ideal gas law

$$\Delta(PV) = \Delta(nRT) \tag{5.15}$$

The method gives the gross heat of combustion—that is, in which the reactants and products are in their standard states. The net heat of combustion, on the other hand, refers to the situation in which the products are in the sate in which they are formed. For Reaction 5.R1, for example, water is formed in the gaseous phase so that the amount of energy released is less than the gross heat of combustion by an amount equivalent to the latent heat of evaporation of water (2.26 kJ/g). The net heat of combustion is the value that should be used in fire calculations. This is illustrated in the next section: see Reactions 5.R5a and 5.R5b. It should also be remembered that there is a heat of gasification associated with any condensed fuel (liquid or solid); a correction must be made for this if the heat of combustion of the fuel vapor is required.

Table 5.3 contains the heats of combustion (ΔH_c) of a number of combustible gases, liquids, and solids, expressed in various ways, viz., kJ/mole (fuel), kJ/g (fuel), kJ/g (oxygen), and kJ/g (air). The first of these is the form normally encountered in chemistry texts and reference books, whereas the second is more commonly found in sources relating to chemical engineering and fuel technology and is more useful to the fire protection engineer. However, the third and, particularly, the fourth have very specific uses in relation to fire problems. It is immediately apparent from Table 5.3 that ΔH_c (O_2) and ΔH_c (air) are approximately constant for most of the fuels listed, having average values of 13.1 kJ/g and 3 kJ/g, respectively. (See the section on "Rate of Heat Release in Fires".)

The data quoted in Table 5.3 refer to heats of combustion measured at ambient temperature, normally 25 °C. These data will be satisfactory for virtually all relevant fire problems, but occasionally it may be necessary to consider the heat released when combustion takes place at higher temperatures. This requires a simple application of the first law of thermodynamics. If the reaction involves reactants at temperature T_0 reacting to give products at the final temperature T_F, the process can be regarded in two ways:

1. The products are formed at T_0, absorb the heat of combustion, and are heated to the final temperature T_F.
2. The heat of combustion is imagined first to heat the reactants to T_F, then the reaction proceeds to completion, with no further temperature rise.

   By the first law, we can write

$$\begin{aligned}(\Delta H_c)^{T_0} &+ C_p^{\mathrm{Pr}} \cdot (T_F - T_0) \\ &= (\Delta H_c)^{T_F} + C_p^{\mathrm{R}} \cdot (T_F - T_0)\end{aligned} \tag{5.16}$$

where C_p^{Pr} and C_p^{R} are the total heat capacities of the products and reactants, respectively. This may be rearranged to give

Table 5.3 Heats of combustion of selected fuels at 25 °C (298 K) [7]

Fuel	ΔH_c (kJ/mol)	ΔH_c (kJ/g)	ΔH_c[b] (kJ/g[O_2])	ΔH_c (kJ/g[air])
Carbon monoxide (CO)	283	10.10	17.69	4.10
Methane (CH_4)	800	50.00	12.54	2.91
Ethane (C_2H_6)	1423	47.45	11.21	2.96
Ethene (C_2H_4)	1411	50.53	14.74	3.42
Ethyne (C_2H_2)	1253	48.20	15.73	3.65
Propane (C_3H_8)	2044	46.45	12.80	2.97
n-Butane (n-C_4H_{10})	2650	45.69	12.80	2.97
n-Pentane (n-C_5H_{12})	3259	45.27	12.80	2.97
n-Hexane	3861	44.90		
c-Hexane (c-C_6H_{12})	3680	43.81	12.80	2.97
n-Octane (n-C_8H_{18})	5104	44.77	12.80	2.97
Benzene (C_6H_6)	3120	40.00	13.06	3.03
Methanol (CH_3OH)	635	19.83	13.22	3.07
Ethanol (C_2H_5OH)	1232	26.78	12.88	2.99
Acetone (CH_3COCH_3)	1786	30.79	14.00	3.25
D-glucose ($C_6H_{12}O_6$)	2772	15.40	13.27	3.08
Cellulose[c]	—	16.09	13.59	3.15
Polyethylene	—	43.28	12.65	2.93
Polypropylene	—	43.31	12.66	2.94
Polystyrene	—	39.85	12.97	3.01
Polyvinylchloride	—	16.43	12.84	2.98
Polymethylmethacrylate	—	24.89	12.98	3.01
Polyacrylonitrile	—	30.80	13.61	3.16
Polyoxymethylene	—	15.46	14.50	3.36
Polyethyleneterephthalate	—	22.00	13.21	3.06
Polycarbonate	—	29.72	13.12	3.04
Nylon 6,6	—	29.58	12.67	2.94
Polyester	—	23.8	—	—
Wool	—	20.5	—	—
Wood (European beech)	—	19.5	—	—
Wood volatiles (European beech)	—	16.6	—	—
Wood char (European beech)	—	34.3	—	—
Wood (Ponderosa pine)	—	19.4	—	—

[a] Apart from the solids (D-glucose, et seq.), the initial state of the fuel and of all the products is taken to be gaseous
[b] $\Delta H_c(O_2) = 13.1$ kJ/g is used in the oxygen consumption method for calculating rate of heat release
[c] Cotton and rayon are virtually pure cellulose and can be assumed to have the same heat of combustion

$$\frac{(\Delta H_c)^{T_F} - (\Delta H_c)^{T_0}}{T_F - T_0} = \Delta C_p \tag{5.17}$$

or, in differential form, we have Kirchoff's equation

$$\frac{d(\Delta H_c)}{dT} = \Delta C_p \tag{5.18}$$

where $\Delta C_p = C_p^{\mathrm{Pr}}\text{-}C_p^{\mathrm{R}}$. This may be used in integrated form to calculate the heat of combustion at temperature T_2 if ΔH_c is known at temperature T_1 and information is available on the heat capacities of the reactants and products, thus

$$(\Delta H_c)^{T_2} = (\Delta H_c)^{T_1} + \int_{T_1}^{T_2} \Delta C_p \cdot dT \tag{5.19}$$

Where

$$\Delta C_p = \sum C_p(\text{products}) - \sum C_p(\text{reactants}) \tag{5.20}$$

and C_p is a function of temperature, which can normally be expressed as a power series in T, for example,

$$C_p = a + bT + cT^2 + \ldots \tag{5.21}$$

Information on heat capacities of a number of species and their variation with temperature may be found in Stull and Prophet [7] and Strehlow [8]. Some data are summarized in Table 5.2.

Heats of Formation

The first law of thermodynamics implies that the change in internal energy (or enthalpy) of a system depends only on the initial and final states of the system and is thus independent of the intermediate stages. This is embodied in thermochemistry as Hess's law, which applies directly to chemical reactions. From this, we can develop the concept of heat of formation, which provides a means of comparing the relative stabilities of different chemical compounds and may be used to calculate heats of chemical reactions that cannot be measured directly.

The heat of formation of a compound is defined as the enthalpy change when 1 mole of that compound is formed from its constituent elements in their standard state (at 1 atm pressure and 298 K). Thus, the heat of formation of liquid water is the enthalpy change of the reaction (at 298 K)

$$\begin{aligned} H_2(\mathrm{g}) + 0.5\mathrm{O}_2(\mathrm{g}) &\rightarrow \mathrm{H_2O(l)}\Delta H_f \\ &= -285.8\,\mathrm{kJ/mol} \end{aligned} \tag{5.R5a}$$

so that ΔH_f (H_2O) (l) = −285.8 kJ/mole at 25 °C. This differs from the heat released by the reaction if the product is water vapor rather than liquid ("The heat of formation of water vapor" kJ/mol [ΔH_f $\{H_2O(g)\} = -241.84$ kJ/mol]) by the latent heat of evaporation of water at 25 °C (43.96 kJ/mol). Thus

$$\begin{aligned} \mathrm{H_2(g)} + 0.5\mathrm{O_2(g)} &\rightarrow \mathrm{H_2O(g)}\Delta H_f[\mathrm{H_2O(g)}] \\ &= -241.84\ \mathrm{kJ/mol} \end{aligned} \tag{5.R5b}$$

By definition, the heats of formation of all the elements are set arbitrarily to zero at all temperatures. This then allows the heats of reaction to be calculated from the heats of formation of the reactants and products, thus

$$\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants}) \tag{5.22}$$

where ΔH is the heat (enthalpy) of the relevant reaction. However, most heats of formation cannot be obtained as easily as heats of combustion. The example given in Reaction (5.R5a) is unusual in that the heat of formation of water also happens to be the heat of combustion of hydrogen. Similarly, the heat of combustion of carbon in its most stable form under ambient conditions (graphite) is the heat of formation of carbon dioxide.

Combustion calorimetry can be used indirectly to calculate heats of formation. The heat of formation of ethyne (acetylene), which is the enthalpy change of the reaction

$$2\mathrm{C(graphite)} + \mathrm{H_2} \rightarrow \mathrm{C_2H_2} \tag{5.R6}$$

can be deduced in the following way: the heat of combustion of ethyne has been determined by bomb calorimetry as −1255.5 kJ/mol at 25 °C (298 K). This is the heat of the reaction

$$\mathrm{C_2H_2} + 2.5\mathrm{O_2} \rightarrow 2\mathrm{CO_2} + \mathrm{H_2O} \tag{5.R7}$$

which, by Hess's law (see Equation 5.22), can be equated to

$$\begin{aligned} (\Delta H_c)^{298}(\mathrm{C_2H_2}) &= 2\left(\Delta H_f\right)^{298}(\mathrm{CO_2}) \\ &+ \left(\Delta H_f\right)^{298}(\mathrm{H_2O}) - \left(\Delta H_f\right)^{298}(\mathrm{C_2H_2}) \\ &- 2.5\left(\Delta H_f\right)^{298}(\mathrm{O_2}) \end{aligned} \tag{5.23}$$

We know that

$$(\Delta H_c)^{298}\ (\mathrm{C_2H_2}) = -1255.5\ \mathrm{kJ/mol}$$
$$(\Delta H_f)^{298}\ (\mathrm{CO_2}) = -393.5\ \mathrm{kJ/mol}$$

$$(\Delta H_f)^{298}\ (H_2O) = -241.8\ \text{kJ/mol}$$

$$(\Delta H_f)^{298}\ (O_2) = 0.0\ \text{kJ/mol (by definition)}$$

so that by rearrangement, Equation 5.23 yields

$$(\Delta H_f)^{298}\ (C_2H_2) = +226.7\ \text{kJ/mol}$$

This compound has a positive heat of formation, unlike CO_2 and H_2O. This indicates that it is an endothermic compound and is therefore less stable than the parent elements. Under appropriate conditions, ethyne can decompose violently to give more stable species.

The heats of formation of a number of compounds are given in Table 5.4. The most stable compounds (CO_2 and H_2O) have the largest negative values, while positive values tend to indicate an instability with respect to the parent elements. This can indicate a high chemical reactivity, and indeed heats of formation have been used in preliminary hazard assessment to provide an indication of the risks associated with new processes in the chemical industry. It should be noted that the heats of combustion of endothermic compounds do not give any indication of any associated reactivity (compare ethane, ethene, and ethyne in Tables 5.3 and 5.4).

Table 5.4 Heats of formation at 25 °C (298 K)

Compound	(ΔH_f)298 (kJ/mol)
Hydrogen (atomic)	+218.00
Oxygen (atomic)	+249.17
Hydroxyl (OH)	+38.99
Chlorine (atomic)	+121.29
Carbon monoxide	–110.53
Carbon dioxide	–393.52
Water (liquid)	–285.8
Water (vapor)	–241.83
Hydrogen chloride	–92.31
Hydrogen cyanide (gas)	+135.14
Nitric oxide	+90.29
Nitrogen dioxide	+33.85
Ammonia	–45.90
Methane	–74.87
Ethane	–84.5
Ethene	+52.6
Ethyne (acetylene)	+226.9
Propane	–103.6
n-Butane	–124.3
Iso-butane[a]	–131.2
Methanol	–242.1

[a] Heats of formation of other hydrocarbons are tabulated in Weast [9]

Rate of Heat Release in Fires

Although thermochemistry can give information relating to the total amount of energy that can be released when a fuel is burned to completion, it is rarely (if ever) possible to use heats of combustion directly to calculate the heat released in "real" fires. Indeed, it can be argued that the *rate* of heat release is more important than the total available [10]. When a single item is burning in isolation, the rate of burning and the rate of heat release in the flame are coupled. It has been common to express the rate of heat release as the product of the burning rate (i.e., the rate of mass loss $\dot{m}$ [kg/s]) and the net heat of combustion of the fuel (ΔH_c kJ/kg).

$$\dot{Q}_c = \dot{m} \cdot \Delta H_c \tag{5.24}$$

However, this assumes that combustion is complete, although it is known that this is never so in natural fires, which involve diffusion flames rather than premixed flames. Air and fuel have to mix by the process of diffusion (laminar or turbulent, depending on the size of the fire) before combustion can occur. The mixing process is relatively inefficient, and despite the fact that excess air is drawn (or *entrained*) into the flame, the products of combustion will contain some species that are only partially oxidized, such as carbon monoxide, aldehydes, ketones, and particulate matter in the form of soot or smoke. Their presence indicates that not all the available combustion energy has been released. The "combustion efficiency" is likely to vary from around 0.3–0.4 for heavily fire-retarded materials to 0.9 or higher in the case of oxygen-containing products (e.g., polyoxymethylene) [10, 11]. This is discussed in detail by Tewarson [12].

Fires burning in compartments present a completely different problem. In the first place, there is likely to be a range of different fuels present, each with a different stoichiometric air requirement. These will burn at different rates, dictated not just by the nature of the fuel but also by the levels of radiant heat existing within the compartment during the fire. The rate of heat release during the fully developed stage of a compartment fire is required for calculating postflashover temperature-time histories for estimating fire exposure of elements of structure, as in the method developed by Pettersson et al. [13]. To calculate the rate of heat release within the compartment, it is assumed that the fire is ventilation controlled and that all combustion takes place within the compartment. The rate of heat release ($\dot{Q}_c$) can be obtained from the expression

$$\dot{Q}_c = \dot{m}_{\text{air}} \cdot \Delta H_c(\text{air}) \tag{5.25}$$

where ΔH_c (air) is the heat of combustion per unit mass of air consumed (3 kJ/g; see Table 5.3), and $\dot{m}_{\text{air}}$ is the mass flow rate of air into the compartment, given approximately by the expression

$$\dot{m}_{\text{air}} = 0.52 A_0 H_0^{1/2} \tag{5.26}$$

where A_0 is the effective area of ventilation (m^2) and H_0 is the height of the ventilation opening (m) [14]. The compartment temperature (as a function of time) is then obtained from heat balance calculations, as described in Drysdale [3], Tewarson [12], and Walton and Thomas [14].

The assumption behind Equation 5.25 is that the burning process is stoichiometric and that all the fuel vapors are burned within the compartment—air is supplied at exactly the rate required to consume the fuel vapors, that is,

$$\frac{\text{Rate of supply of air}}{\text{Rate of supply of fuel}} = r$$

where r is the stoichiometric air-fuel ratio and the maximum possible temperatures will be achieved. However, it is worth noting that this does not take into account the fact that the rate of heat release is not instantaneous. Although (in principle) the ideal stoichiometric mixture is created within the compartment, burning gases will emerge from the opening(s) simply because the reaction takes time to reach completion. Burning gases (i.e., flames) are carried outside the compartment, indicating that not all of the heat of combustion is released within the compartment. For a fully developed (postflashover) fire, it is perhaps more likely that the ratio $\dot{m}_{\text{air}}/\dot{m}_{\text{fuel}}$ (the "equivalence ratio") is less than the stoichiometric ratio r—that is, insufficient air is entering the compartment to burn all the fuel vapors. Under these circumstances, excess fuel vapors will escape from the compartment and burn outside as they mix with external air. The external flame length will depend *inter alia* on the equivalence ratio [15].

Regardless of whether the equivalence ratio is equal to or greater than the stoichiometric ratio, fuel vapor will burn outside the compartment and temperatures based on Equation 5.25 will be high. The method will also overestimate the temperatures achieved if the equivalence ratio is much greater than the stoichiometric ratio. Under these conditions, excess air is drawn into the compartment and will act as a diluent and reduce the average temperatures—if the ventilation is high enough, the rate of heat release will be controlled by the area of the burning surface [3, 16].

Note that the concept of equivalence ratio is used elsewhere in this handbook, specifically by Tewarson [12] and by Gottuk and Lattimer [17] in discussing the yields of products generated in the upper layer during the preflashover fire.

Much useful data on the fire behavior of combustible materials can be obtained by using the technique of "oxygen consumption calorimetry." This is the basis of the "cone calorimeter," in which the rate of heat release from a small sample of material burning under an imposed radiant heat flux is determined by measuring the rate of oxygen consumption [18]. The latter can be converted into a rate of heat release using the conversion factor 13.1 kJ/g of oxygen consumed. (A small correction is required for incomplete combustion, based on the yield of CO.) This technique can be used on a larger scale to measure the rate of heat release from items of furniture, wall lining materials, and so on [19, 20] and is now used routinely in both fire research and fire testing facilities.

Calculation of Adiabatic Flame Temperatures

In the previous sections, no consideration has been given to the fate of the energy released by the combustion reactions. Initially it will be absorbed within the reaction system itself by (1) unreacted reactants, (2) combustion products, and (3) diluents, although it will ultimately be lost from the system by various heat transfer processes. This is particularly true for natural fires in enclosed spaces. However, if we consider a premixed reaction system, such as a flammable vapor-air mixture, and assume it to be adiabatic, that is, there is no transfer of heat (or mass) to or from the system, then we can calculate the maximum theoretical temperature, the adiabatic flame temperature.

Consider a flame propagating through a stoichiometric propane-air mixture of infinite extent (i.e., there are no surfaces to which heat may be transferred) and that is initially at 25 °C. The appropriate equation is given by Reaction 5.R8:

$$\begin{aligned} &C_3H_8 + 5O_2 + 18.8N_2 \rightarrow \\ &\quad 3CO_2 + 4H_2O + 18.8N_2 \end{aligned} \tag{5.R8}$$

This reaction releases 2044 kJ for every mole of propane consumed. This quantity of energy goes toward heating the reaction products, that is, 3 moles of carbon dioxide, 4 moles of water (vapor), and 18.8 moles of nitrogen for every mole of propane burned. The thermal capacity of this mixture can be calculated from the thermal capacities of the individual gases, which are available in the literature (e.g., JANAF) [7]. The procedure is straightforward, provided that an average value of C_p is taken for each gas in the temperature range involved, giving 942.5 kJ/K as the total thermal capacity of the products per mole of propane consumed (see Table 5.5).

As 2044 kJ are released at the same time as these species are formed, the maximum temperature rise will be

Table 5.5 Thermal capacity of the products of combustion of a stoichiometric propane/air mixture

	No. of moles	Thermal capacity at 1000 K (J/mol·K)	Thermal capacity at 1000 K (J/K)
CO_2	3	54.3	162.9
H_2O	4	41.2	164.8
N_2	18.8	32.7	614.8
	Total thermal capacity (per mole of propane)	=	942.5 J/K

$$\Delta T = \frac{2044000}{942.5} = 2169 \text{ K}$$

giving the final (adiabatic) temperature as 2169 + 298 = 2467 K. In fact, this figure is approximate for the following reasons:

1. Thermal capacities change with temperature, and average values over the range of temperatures appropriate to the problem have been used.
2. The system cannot be adiabatic as there will be heat loss by radiation from the hot gases (CO_2 and H_2O).
3. At high temperatures, dissociation of the products will occur; as these are endothermic processes, there will be a reduction in the final temperature.

Of these, (2) and (3) determine that the actual flame temperature will be much lower than predicted. These effects can be taken into account. Thus, with propane burning in air, the final temperature may not exceed 2000 K.

If the propane were burning as a stoichiometric mixture in pure oxygen, then in the absence of nitrogen as a "heat sink," much higher temperatures would be achieved. The total thermal capacity would be (942.5 − 614.8) = 327.7 J/K. However, the amount of heat released remains unchanged (2044 kJ) so that the maximum temperature rise would be

$$\Delta T = \frac{2044000}{327.7} = 6238\text{K}$$

predicting a final temperature of 6263 °C. Because dissociation will be a dominant factor, this cannot be achieved and the temperature of the flame will not exceed approximately 3500 K.

The occurrence of dissociation at temperatures in the region of 2000 K and above makes it necessary to take dissociation into account. Dissociation is discussed in Chap. 6. However, the simple calculation outlined above can be used to estimate the temperatures of near-limit flames, when the temperature is significantly lower and dissociation can be neglected.

It is known that the lower flammability limit of propane is 2.2 %. The oxidation reaction taking place in this mixture can be described by the following equation:

$$0.022C_3H_8 + 0.978(0.21O_2 + 0.79N_2) \rightarrow \text{products}$$

Dividing through by 0.022 allows this to be written

$$\begin{aligned} C_3H_8 + 9.34O_2 + 35.12N_2 &\rightarrow 3CO_2 + 4H_2O \\ &+ 4.34O_2 + 35.12N_2 \end{aligned} \qquad (5.R9)$$

showing that the heat released by the oxidation of 1 mole of propane is now absorbed by excess oxygen (4.34 moles) and an increased amount of nitrogen as well as the combustion products. Carrying out the same calculation as before, it can be shown that the total thermal capacity of the products per mole of propane consumed is 1627.6 kJ/K, which gives the adiabatic flame temperature for this limiting mixture is 1281 °C (1554 K). If the same calculation is carried out for the other hydrocarbon gases, it is found that the adiabatic limiting flame temperature lies in a fairly narrow band, 1600 ± 100 K (Table 5.6). This can be interpreted by assuming that the limit exists because heat losses (by radiation from the flame) exceed the rate of heat production (within the flame). As a consequence, flame cannot sustain itself. This concept can be applied to certain practical problems relating to the lower flammability limit.

Table 5.6 Adiabatic flame temperature of lower-limiting hydrocarbon/air mixtures

Gas	Adiabatic flame temperature at lower flammability limit (K)
Methane	1446
Ethane	1502
Propane	1554
n-Butane	1612
n-Pentane	1564
n-Heptane	1692
n-Octane	1632

Example 1 It is recognized that the leak of propane into a test cell could lead to a flammable atmosphere, and it is decided to keep the atmosphere inert by the addition of nitrogen. Calculate the percentage of nitrogen necessary to prevent ignition of a mixture in which the propane and air are in stoichiometric proportions.

Solution The stoichiometric reaction for propane in air is

$$\begin{aligned} C_3H_8 + 5O_2 + 18.8N_2 \rightarrow \\ 3CO_2 + 4H_2O + 18.8N_2 \end{aligned} \qquad (5.R10)$$

and the heat of combustion of propane is 2044 kJ/mole. It is assumed that the heat of combustion is absorbed by the products $3CO_2$ + $4H_2O$ + 18.8 N_2. It was shown above that the adiabatic flame temperature (i.e., the temperature of the product gases, assuming no heat losses) will be 2169 K. If the flame temperature can be held below 1600 K (or 1554 K, according to Table 5.6), then flame propagation will not be possible and the introduction of an ignition source will not lead to an explosion. Suppose that the extra quantity of nitrogen required to form an "inert atmosphere" corresponds to X moles per mole of propane. Then

$$\begin{aligned} C_3H_8 + 5O_2 + 18.8N_2 + XN_2 \\ \rightarrow 3CO_2 + 4H_2O + (18.8 + X)N_2 \end{aligned} \qquad (5.R11)$$

Following the procedure illustrated in Table 5.5, the thermal capacity of the product gases—$3CO_2$ + $4H_2O$ + $(18.8 + X)N_2$—will be 3 × 54.3 + 4 × 41.2 + (18.8 + X) × 32.7 = ΣC_p. If sufficient nitrogen has been added to reduce the adiabatic flame temperature to 1554 K, then the thermal capacity of the product gases will be given by

$$\sum C_p = \frac{2044000}{1554 - 298}$$
$$= 1627.4\,\text{kJ/mole of propane}$$

Thus

$$3 \times 54.3 + 4 \times 41.2 + (18.8 + X) \times 32.7 = 1627.4$$

$$X = 20.9$$

Consequently, the amount of nitrogen added to the air in the test cell to render the atmosphere "inert" with respect to a leak of propane corresponds to 20.9 moles of N_2 for every (5 + 18.8) = 23.8 moles of air, that is, the mixture in the cell must be 47 % nitrogen, the balance being air. (Experimentally, a significantly lower figure is obtained—c. 40 %. It should be remembered that in the above calculation it is assumed that the adiabatic temperature assumption is valid and that the reaction will go to completion.)

Example 2 A mechanical engineering research laboratory contains a six-cylinder internal combustion engine that is being used for research into the performance of spark plugs. The fuel being used is methane, CH_4, and the fuel-air mixture can be adjusted at will. The combustion products are extracted from the exhaust manifold through a 30 cm square duct, 20 m long. It is found that the engine will continue to operate with a stoichiometric mixture when only three of the cylinders are firing. If under these conditions the average temperature of the gases entering the duct from the manifold is 700 K, is there a risk of an explosion in the duct?

Solution The stoichiometric reaction for methane in air is

$$CH_4 + 2O_2 + 7.52N_2 \rightarrow CO_2 + 2H_2O + 7.52N_2 \tag{5.R12}$$

If we consider that 1 mole of fuel passes through each of the six cylinders, but of the 6 moles only three are burned, we have overall

$$6CH_4 + 12O_2 + 45.12N_2 \rightarrow 3CH_4 + 3CO_2 + 6H_2O + 6O_2 + 45.12N_2 \tag{5.R13}$$

Dividing through by 3 gives

$$2CH_4 + 4O_2 + 15.04N_2 \rightarrow CH_4 + 2O_2 + CO_2 + 2H_2O + 15.04N_2 \tag{5.R14}$$

The mixture discharged into the exhaust manifold has the composition given by the right-hand side of Reaction 5.R14. If this "burns" at 700 K, the final abiabatic flame temperature may be calculated on the basis of the reaction

$$CH_4 + 2O_2 + CO_2 + 2H_2O + 15.04N_2 \rightarrow 2CO_2 + 4H_2O + 15.04N_2 \tag{5.R15}$$

The total thermal capacity of the product gases ($2CO_2 + 4H_2O + 15.04\ N_2$) (at 1000 K) can be shown to be 765.3 J per mole of methane burned. Using Kirchoff's equation (Equation 5.19), $\Delta H_c(CH_4)$ at 700 K is calculated as 802.8 kJ/mol, giving $\Delta T = 802800/765.3 = 1049$ K. This gives a final temperature of 1749 K, which is significantly higher than the limiting flame temperature (1600 K) discussed above. This indicates that there is a risk of explosion, and measures should be applied to prevent this mixture being discharged into the duct.

It should be noted that at 700 K there will be a "slow" reaction between methane and the oxygen present, which could invalidate the tacit assumption that the duct becomes completely filled with the mixture described by the right-hand side of Reaction 5.R13. However, slow oxidation of the methane will tend to make the mixture less flammable, and so the calculation gives a conservative answer.

Nomenclature

A	Area (Equation 5.5)
A_w	Area of ventilation opening
C_p	Specific heat
E	Internal energy
F	Force (Equation 5.4)
H	Height of ventilation opening
H	Enthalpy
ΔH_c	Heat of combustion
ΔH_f	Heat of formation
$\dot{m}$	Mass rate of burning
$\dot{m}_{\text{air}}$	Mass flow rate of air
n	Number of moles
p	Pressure
q	Energy
Q_c	Rate of heat release
R	Universal gas constant
T	Temperature
V	Volume
w	Work

Subscripts

c	Combustion
F	Final
f	Formation
o	Initial
p	Constant pressure
v	Constant volume

Superscripts

Pr	Products
R	Reactants

References

1. W.J. Moore, *Physical Chemistry,* 5th ed., Longman, London (1974).
2. P Atkins and J de Paula, “Atkins’ Physical Chemistry” 9th Edition (Oxford University Press, 2009)
3. D.D. Drysdale, *Introduction to Fire Dynamics,* 3rd ed., John Wiley and Sons, Chichester, UK (2011).
4. J.F. Griffiths, “Combustion Kinetics,” in *SFPE Handbook of Fire Protection Engineering,* 4th ed. (P.J. DiNenno et al., eds.), National Fire Protection Association, Quincy, MA, pp. 1-220–1-230 (2008).
5. A.F. Roberts, *Combustion and Flame,* 8, p. 245 (1964).
6. G M Barrow, “*Physical Chemistry*” 4th Edition, McGraw-Hill Book Co. (New York, 1961)
7. NIST-JANAF *Thermochemical Tables*: see http://kinetics.nist.gov/janaf/
8. R.A. Strehlow, *Combustion Fundamentals,* McGraw-Hill, New York (1984).
9. R.C. Weast, *Handbook of Chemistry and Physics,* Chemical Rubber Co., Cleveland, OH (1973).
10. V. Babrauskas and R. Peacock, “Heat Release Rate: The Single Most Important Variable in Fire Hazard,” in *Fire Safety Journal,* 18, pp. 255–272 (1992).
11. A. Tewarson, in *Flame Retardant Polymeric Materials* (M. Lewin, ed.), Plenum, New York (1982).
12. M. Khan, A. Tewarson, and M. Chaos, “Combustion Characteristics of Materials and Generation of Fire Products,” in *SFPE Handbook of Fire Protection Engineering,* 5th ed. Springer, New York, 2015.
13. O. Pettersson, S.E. Magnusson, and J. Thor, *Fire Engineering Design of Structures,* Swedish Institute of Steel Construction, Publication, 50 (1976).
14. W.D. Walton and P.H. Thomas, “Estimating Temperatures in Compartment Fires,” in *SFPE Handbook of Fire Protection Engineering,* 4th ed. (P.J. DiNenno et al., eds.), Society of Fire Protection Engineers, Bethesda, MD, pp. 3-204–3-221 (2008).
15. M.L. Bullen and P.H. Thomas, *Seventeenth Symposium (International) on Combustion,* Combustion Institute, Pittsburgh, PA (1979).
16. P.H. Thomas and A.J.M. Heselden, “Fully Developed Fires in Compartments,” *CIB Report No. 20; Fire Research Note No. 923,* Conseil International du Batiment, France (1972).
17. D.T. Gottuk and B.Y. Lattimer, “Effect of Combustion Conditions on Species Production,” in *SFPE Handbook of Fire Protection Engineering,* 4th ed. (P.J. DiNenno et al., eds.), National Fire Protection Association, Quincy, MA, pp. 2-67–2-95 (2008).
18. V. Babrauskas, “The Cone Calorimeter,” in *SFPE Handbook of Fire Protection Engineering,* 4th ed. (P.J. DiNenno et al., eds.), National Fire Protection Association, Quincy, MA, pp. 3-90–3-108 (2008).
19. V. Babrauskas and S.J. Grayson (eds.), *Heat Release in Fires,* Elsevier Applied Science, London (1992).
20. M.L. Janssens, “Calorimetry,” in *SFPE Handbook of Fire Protection Engineering,* 5th ed. Springer, 2015.

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