Chapter 14:

CHEMICAL REACTIONS

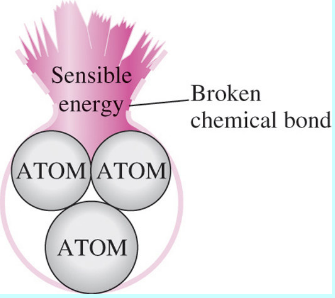
ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

We mentioned in previous chapters that the molecules of a system possess energy in various forms such as:
sensible and *latent energy* (associated with a change of state),
chemical energy (associated with the molecular structure), and
nuclear energy (associated with the atomic structure).

During a chemical reaction, some chemical bonds that bind the atoms into molecules are broken, and new ones are formed.

The chemical energy associated with these bonds, in general, is different for the reactants and the products.

Therefore, a process that involves chemical reactions involves changes in chemical energies, which must be accounted for in an energy balance .



ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

Assuming the atoms of each reactant remain intact (no nuclear reactions) and disregarding any changes in kinetic and potential energies, the energy change of a system during a chemical reaction is due to a change in state and a change in chemical composition. That is:

$$\Delta E_{\text{sys}} = \Delta E_{\text{state}} + \Delta E_{\text{chem}}$$

Therefore, when the products (formed during a chemical reaction) exit the reaction chamber at the inlet state of the reactants, we have $\Delta E_{\text{state}} = 0$ and the energy change of the system in this case is due to the changes in its chemical composition only.

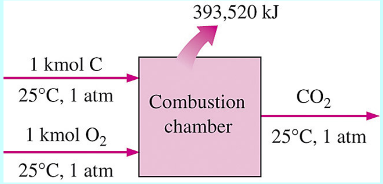
ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

Consider the formation of CO_2 from its elements, carbon and oxygen, during a steady-flow combustion process (see Figure).

Both the carbon and the oxygen enter the combustion chamber at 25°C and 1 atm. The CO_2 formed during this process also leaves the combustion chamber at 25°C and 1 atm. (same state)

The combustion of carbon is an *exothermic reaction* (a reaction during which chemical energy is released in the form of heat).

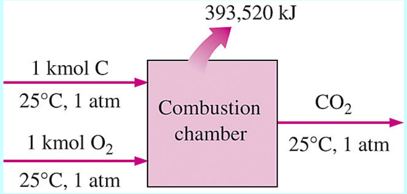
Therefore, some heat is transferred from the combustion chamber to the surroundings during this process, which is 393,520 kJ/kmol CO_2 formed.



(When one is dealing with chemical reactions, it is more convenient to work with quantities per unit mole than per unit time, even for steady-flow processes.)

ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

The process described here involves no work interactions.



Therefore, from the steady-flow energy balance relation, the heat transfer during this process must be equal to the difference between the enthalpy of the products and the enthalpy of the reactants. That is,

$$Q = H_{\text{prod}} - H_{\text{react}} = -393{,}520 \text{ kJ/kmol}$$

Since both the reactants and the products are at the same state, the enthalpy change during this process is solely due to the changes in the chemical composition of the system.

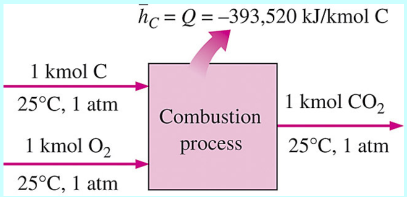
This enthalpy change is different for different reactions, and it is very desirable to have a property to represent the changes in chemical energy during a reaction.

ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

This property is the **enthalpy of reaction** h_R, which is defined as *the difference between the enthalpy of the products at a specified state and the enthalpy of the reactants at the same state for a complete reaction.*

For combustion processes, the enthalpy of reaction is usually referred to as the **enthalpy of combustion** h_C, which represents the amount of heat released during a steady-flow combustion process when 1 kmol (or 1 kg) of fuel is burned completely at a specified temperature and pressure (see Figure). It is expressed as:

$$h_R = h_C = H_{\text{prod}} - H_{\text{react}}$$



which is -393,520 kJ/kmol for C at the standard reference state.

The enthalpy of combustion of a particular fuel is different at different temperatures and pressures.

ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

The enthalpy of combustion is obviously a very useful property for analyzing the combustion processes of fuels.

However, there are so many different fuels and fuel mixtures that it is not practical to list h_C values for all possible cases.

Besides, the enthalpy of combustion is not of much use when the combustion is incomplete.

Therefore a more practical approach would be to have a more fundamental property to represent the chemical energy of an element or a compound at some reference state.

This property is the **enthalpy of formation** h^o_f, which can be viewed as *the enthalpy of a substance at a specified state due to its chemical composition*.

ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

To establish a starting point, we assign the enthalpy of formation of all stable elements (such as O_2, N_2, H_2, and C) a value of zero at the standard reference state of 25°C and 1 atm.

That is, $h^o_f = 0$ for all stable elements. (This is no different from assigning the internal energy of saturated liquid water a value of zero at 0.01°C.)

Perhaps we should clarify what we mean by *stable*.

The stable form of an element is simply the chemically stable form of that element at 25°C and 1 atm.

Nitrogen, for example, exists in diatomic form (N_2) at 25°C and 1 atm.

Therefore, the stable form of nitrogen at the standard reference state is diatomic nitrogen N_2, not monatomic nitrogen N.

ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

Now reconsider the formation of CO_2 (a compound) from its elements C and O_2 at 25°C and 1 atm during a steady-flow process. The enthalpy change during this process was determined to be -393,520 kJ/kmol.

However, $H_{\text{react}} = 0$ since both reactants are elements at the standard reference state, and the products consist of 1 kmol of CO_2 at the same state.

Therefore, the enthalpy of formation of CO_2 at the standard reference state is -393,520 kJ/kmol. That is,

$$\boxed{\bar{h}^{\circ}_{f,\mathrm{CO_2}} = -393{,}520\ \mathrm{kJ/kmol}}$$

The negative sign is due to the fact that the enthalpy of 1 kmol of CO_2 at 25°C and 1 atm is 393,520 kJ less than the enthalpy of 1 kmol of C and1 kmol of O_2 at the same state.

In other words, 393,520 kJ of chemical energy is released (leaving the system as heat) when C and O_2 combine to form 1 kmol of CO_2.

ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

Substance	Formula	M	$\bar{h}^{o}_{f}$ kJ/kmol
Carbon	C	12	0
Hydrogen	H_2	2	0
Oxygen	O_2	32	0
Nitrogen	N_2	28	0
Carbon dioxide	CO_2	44	-393,520
Carbon monoxide	CO	28	-110,530
Water (vapor)	H_2O (vap)	18	-241,820
Water (liquid)	H_2O (liq)	18	-285,830
Methane	CH_4	16	-74,850
Acetylene	C_2H_2	26	+226,730
Ethane	C_2H_6	30	-84,680
Propane	C_3H_8	44	-103,850
Butane	C_4H_{10}	58	-126,150
Octane (vapor)	C_8H_{18}	114	-208,450
Dodecane	$C_{12}H_{26}$	170	-291,010

ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

You will notice that two $h°_f$ values are given for H_2O in Table A–26, one for liquid water and the other for water vapor.

This is because both phases of H_2O are encountered at 25°C, and the effect of pressure on the enthalpy of formation is small. (Note that under equilibrium conditions, water exists only as a liquid at 25°C *and* 1 atm.)

The difference between the two enthalpies of formation is equal to the h_{fg} of water at 25°C, which is 2441.7 kJ/kg or 44,000 kJ/kmol.

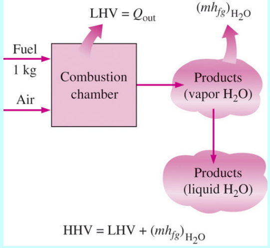
Another term commonly used in conjunction with the combustion of fuels is the **heating value** of the fuel, which is defined as the amount of heat released when a fuel is burned completely in a steady-flow process and the products are returned to the state of the reactants.

In other words, the heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel. That is, $\text{Heating value} = |h_C|$

ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

The heating value depends on the *phase* of the H_2O in the products.

The heating value is called the **higher heating value** (HHV) when the H_2O in the products is in the liquid form, and it is called the **lower heating value** (LHV) when the H_2O in the products is in the vapor form (See Figure).



The two heating values are related by:

$$\text{HHV} = \text{LHV} + (mh_{fg})_{H_2O} \qquad (\text{kJ/kg fuel})$$

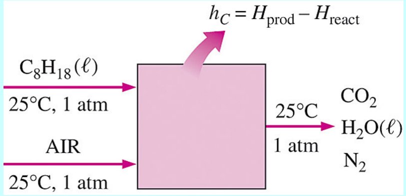
where m is the mass of H_2O in the products per unit mass of fuel and h_{fg} is the enthalpy of vaporization of water at the specified temperature.

Higher and lower heating values of common fuels are given in Table A–27.

The heating value or enthalpy of combustion of a fuel can be determined from a knowledge of the enthalpy of formation for the compounds involved.

EXAMPLE 14–5
Evaluation of the Enthalpy of Combustion

- Determine the enthalpy of combustion of liquid octane (C_8H_{18}) at 25°C and 1 atm, using enthalpy-of-formation data from Table A–26. Assume the water in the products is in the liquid form.



$$C_8H_{18} + a_{th}(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O(\ell) + 3.76a_{th}N_2$$

$$\begin{aligned}\bar{h}_C &= H_{prod} - H_{react}\\ &= \sum N_p\bar{h}^\circ_{f,p} - \sum N_r\bar{h}^\circ_{f,r} = (N\bar{h}^\circ_f)_{CO_2} + (N\bar{h}^\circ_f)_{H_2O} - (N\bar{h}^\circ_f)_{C_8H_{18}}\end{aligned}$$

$$\begin{aligned}\bar{h}_C &= (8\ \text{kmol})(-393{,}520\ \text{kJ/kmol}) + (9\ \text{kmol})(-285{,}830\ \text{kJ/kmol})\\ &\quad -(1\ \text{kmol})(-249{,}950\ \text{kJ/kmol})\\ &= \mathbf{-5{,}471{,}000\ kJ/kmol\ C_8H_{18} = -47{,}891\ kJ/kg\ C_8H_{18}}\end{aligned}$$

ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

In thermodynamics we are concerned with the *changes* in the energy of a system during a process, and not the energy values at the particular states.

Therefore, we can choose any state as the reference state and assign a value of zero to the internal energy or enthalpy of a substance at that state.

When a process involves no changes in chemical composition, the reference state chosen has no effect on the results.

When the process involves chemical reactions, however, the composition of the system at the end of a process is no longer the same as that at the beginning of the process.

In this case it becomes necessary to have a common reference state for all substances.

ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

The chosen reference state is 25°C (77°F) and 1 atm, which is known as the **standard reference state.**

Property values at the standard reference state are indicated by a superscript (°) (such as $h°$ and $u°$).

When analyzing reacting systems, we must use property values relative to the standard reference state.

However, it is not necessary to prepare a new set of property tables for this purpose.

We can use the existing tables by subtracting the property values at the standard reference state from the values at the specified state.

The ideal-gas enthalpy of N_2 at 500 K relative to the standard reference state, for example, is $h_{500\text{ K}} - h° = 14{,}581 - 8669 = 5912$ kJ/kmol.

FIRST-LAW ANALYSIS OF REACTING SYSTEMS

The energy balance (or the first-law) relations developed in previous Chapters are applicable to both reacting and non-reacting systems.

However, chemically reacting systems involve changes in their chemical energy, and thus it is more convenient to rewrite the energy balance relations so that the changes in chemical energies are explicitly expressed.

We do this first for steady-flow systems and then for closed systems.

Steady-Flow System

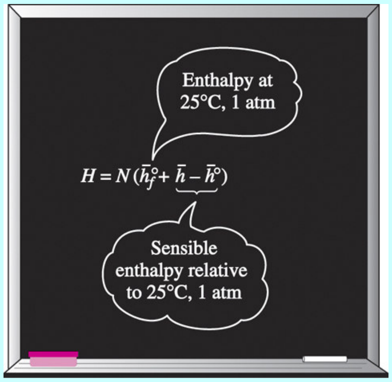
Closed System

FIRST-LAW ANALYSIS OF REACTING SYSTEMS

Steady-Flow System

Before writing the energy balance relation, we need to express the enthalpy of a component in a form suitable for use for reacting systems.

That is, we need to express the enthalpy such that it is relative to the standard reference state and the chemical energy term appears explicitly.



When expressed properly, the enthalpy term should reduce to the enthalpy of formation h°_f at the standard reference state.
With this in mind, we express the enthalpy of a component on a unit mole basis as: (See Figure)

$$\text{Enthalpy} = \bar{h}_f^\circ + (\bar{h} - \bar{h}^\circ) \qquad (\text{kJ/kmol})$$

FIRST-LAW ANALYSIS OF REACTING SYSTEMS

Steady-Flow System

$$\text{Enthalpy} = \bar{h}_f^\circ + (\bar{h} - \bar{h}^\circ) \qquad (\text{kJ/kmol})$$

where the term in the parentheses represents the sensible enthalpy relative to the standard reference state, which is the difference between h the sensible enthalpy at the specified state) and h° (the sensible enthalpy at the standard reference state of 25°C and 1 atm).

This definition enables us to use enthalpy values from tables regardless of the reference state used in their construction.

When the changes in kinetic and potential energies are negligible, the steady-flow energy balance relation $E_{in} = E_{out}$ can be expressed for a *chemically reacting steady-flow system* more explicitly as:

$$\underbrace{Q_{\text{in}} + W_{\text{in}} + \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r}_{\substack{\text{Energy transfer in per mole of fuel} \\ \text{by heat, work, and mass}}} = \underbrace{Q_{\text{out}} + W_{\text{out}} + \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p}_{\substack{\text{Energy transfer out per mole of fuel} \\ \text{by heat, work, and mass}}}$$

FIRST-LAW ANALYSIS OF REACTING SYSTEMS

Steady-Flow System

$$\underbrace{Q_{\text{in}} + W_{\text{in}} + \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r}_{\substack{\text{Energy transfer in per mole of fuel} \\ \text{by heat, work, and mass}}} = \underbrace{Q_{\text{out}} + W_{\text{out}} + \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p}_{\substack{\text{Energy transfer out per mole of fuel} \\ \text{by heat, work, and mass}}}$$

The energy balance relation just discussed can be expressed more compactly as:

$$Q - W = H_{\text{prod}} - H_{\text{react}}$$

$$H_{\text{prod}} = \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p$$

$$H_{\text{react}} = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r$$

The energy balance relations above are sometimes written without the work term since most steady-flow combustion processes do not involve any work interactions.

A combustion chamber normally involves heat output but no heat input.

Then the energy balance for a *typical steady-flow combustion process* becomes:

$$\boxed{Q_{\text{out}} = \underbrace{\sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r}_{\substack{\text{Energy in by mass} \\ \text{per mole of fuel}}} - \underbrace{\sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p}_{\substack{\text{Energy out by mass} \\ \text{per mole of fuel}}}}$$

FIRST-LAW ANALYSIS OF REACTING SYSTEMS

Closed System

The general closed-system energy balance relation $E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$ can be expressed for a stationary *chemically reacting closed system* as:

$$(Q_{\text{in}} - Q_{\text{out}}) + (W_{\text{in}} - W_{\text{out}}) = U_{\text{prod}} - U_{\text{react}}$$

where U_{prod} represents the internal energy of the products and U_{react} represents the internal energy of the reactants.

To avoid using another property— *the internal energy of formation* u^o_f— we utilize the definition of enthalpy

$$\bar{u}_f^\circ + \bar{u} - \bar{u}^\circ = \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v}$$

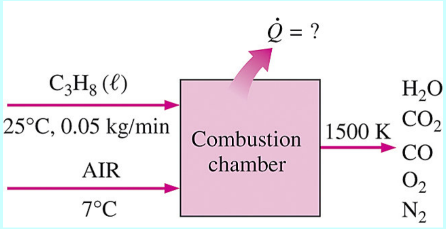
and express the above equation as:

$$Q - W = \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_p - \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v})_r$$

EXAMPLE 14–6

First-Law Analysis of Steady-Flow Combustion

- Liquid propane (C_3H_8) enters a combustion chamber at 25°C at a rate of 0.05 kg/min where it is mixed and burned with 50 percent excess air that enters the combustion chamber at 7°C, as shown. An analysis of the combustion gases reveals that all the hydrogen in the fuel burns to H_2O but only 90 percent of the carbon burns to CO_2, with the remaining 10 percent forming CO. If the exit temperature of the combustion gases is1500 K, determine:
- (*a*) the mass flow rate of air and
- (*b*) the rate of heat transfer from the combustion chamber.



EXAMPLE 14–6

First-Law Analysis of Steady-Flow Combustion

- The theoretical amount of air is determined from the stoichiometric reaction to be:

$$C_3H_8(\ell) + a_{th}(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 3.76a_{th}N_2$$

$$O_2 \text{ balance:} \qquad a_{th} = 3 + 2 = 5$$

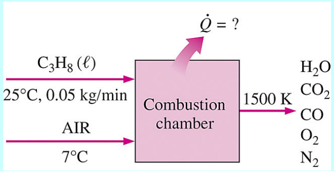
- Then the balanced equation for the actual combustion process with 50 percent excess air and some CO in the products becomes

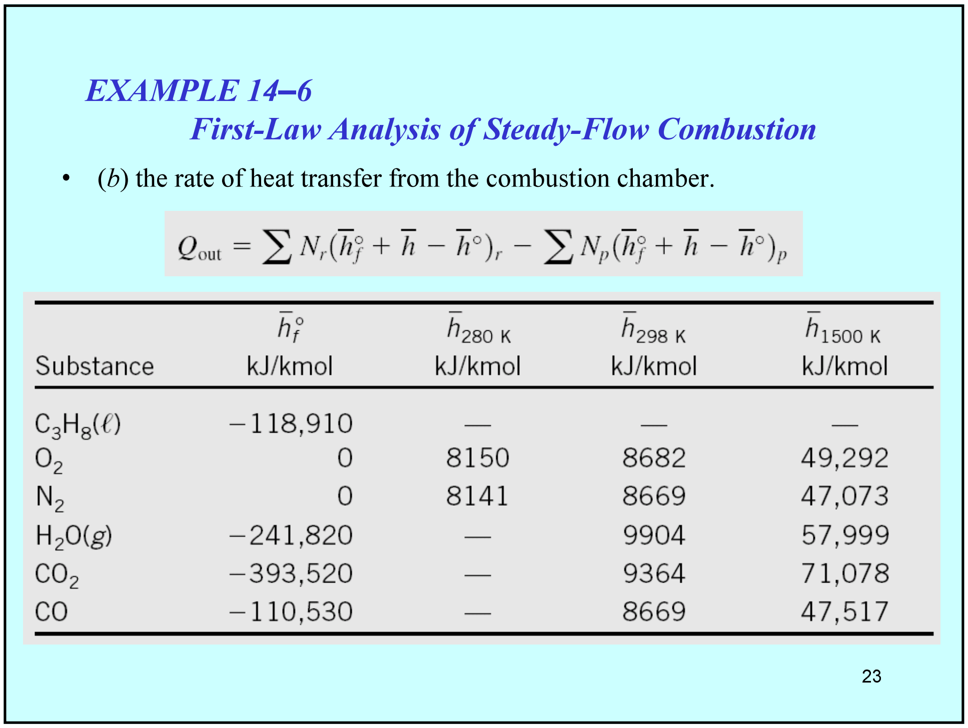
$$C_3H_8(\ell) + 7.5(O_2 + 3.76N_2) \rightarrow 2.7CO_2 + 0.3CO + 4H_2O + 2.65O_2 + 28.2N_2$$

- (*a*) the mass flow rate of air and

$$\text{AF} = \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{(7.5 \times 4.76 \text{ kmol})(29 \text{ kg/kmol})}{(3 \text{ kmol})(12 \text{ kg/kmol}) + (4 \text{ kmol})(2 \text{ kg/kmol})}$$
$$= 25.53 \text{ kg air/kg fuel}$$

$$\dot{m}_{\text{air}} = (\text{AF})(\dot{m}_{\text{fuel}})$$
$$= (23.53 \text{ kg air/kg fuel})(0.05 \text{ kg fuel/min})$$
$$= \mathbf{1.18 \text{ kg air/min}}$$



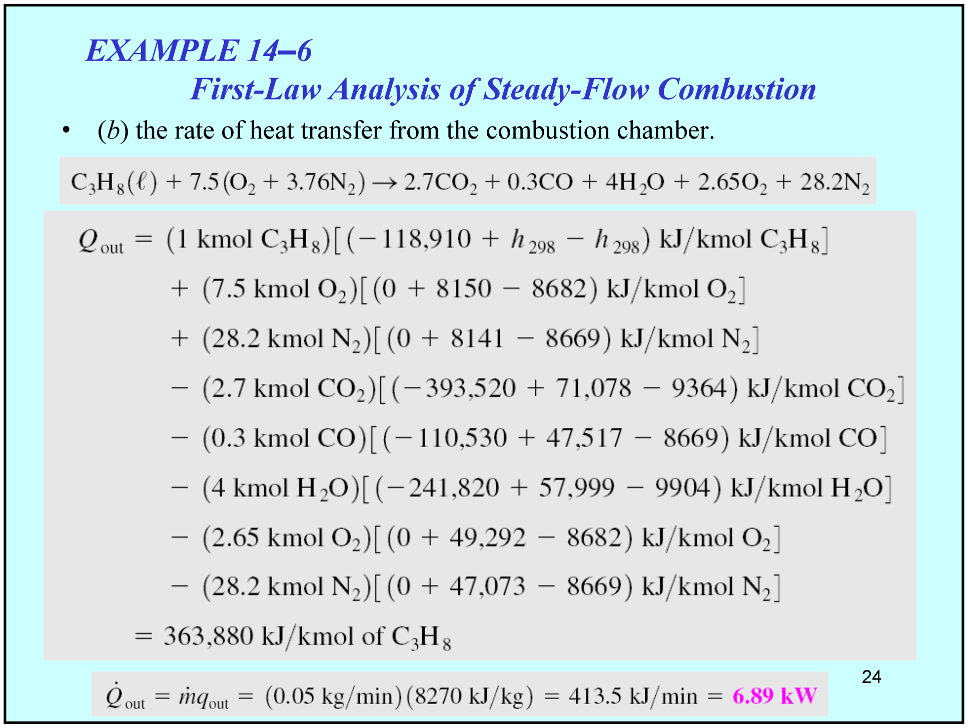


EXAMPLE 14–6
First-Law Analysis of Steady-Flow Combustion

- (*b*) the rate of heat transfer from the combustion chamber.

$$Q_{\text{out}} = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r - \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p$$

Substance	$\bar{h}_f^\circ$ kJ/kmol	$\bar{h}_{280\text{ K}}$ kJ/kmol	$\bar{h}_{298\text{ K}}$ kJ/kmol	$\bar{h}_{1500\text{ K}}$ kJ/kmol
$C_3H_8(\ell)$	−118,910	—	—	—
O_2	0	8150	8682	49,292
N_2	0	8141	8669	47,073
$H_2O(g)$	−241,820	—	9904	57,999
CO_2	−393,520	—	9364	71,078
CO	−110,530	—	8669	47,517



EXAMPLE 14–6
First-Law Analysis of Steady-Flow Combustion

- (*b*) the rate of heat transfer from the combustion chamber.

$$C_3H_8(\ell) + 7.5(O_2 + 3.76N_2) \rightarrow 2.7CO_2 + 0.3CO + 4H_2O + 2.65O_2 + 28.2N_2$$

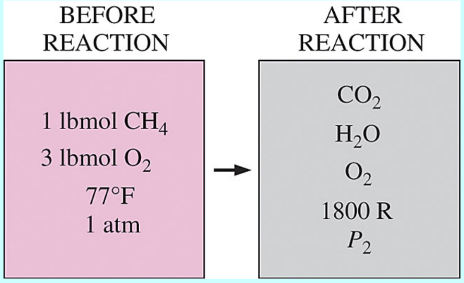
$$\begin{aligned} Q_{\text{out}} = {} & (1\text{ kmol }C_3H_8)[(-118{,}910 + \bar{h}_{298} - \bar{h}_{298})\text{ kJ/kmol }C_3H_8] \\ & + (7.5\text{ kmol }O_2)[(0 + 8150 - 8682)\text{ kJ/kmol }O_2] \\ & + (28.2\text{ kmol }N_2)[(0 + 8141 - 8669)\text{ kJ/kmol }N_2] \\ & - (2.7\text{ kmol }CO_2)[(-393{,}520 + 71{,}078 - 9364)\text{ kJ/kmol }CO_2] \\ & - (0.3\text{ kmol }CO)[(-110{,}530 + 47{,}517 - 8669)\text{ kJ/kmol }CO] \\ & - (4\text{ kmol }H_2O)[(-241{,}820 + 57{,}999 - 9904)\text{ kJ/kmol }H_2O] \\ & - (2.65\text{ kmol }O_2)[(0 + 49{,}292 - 8682)\text{ kJ/kmol }O_2] \\ & - (28.2\text{ kmol }N_2)[(0 + 47{,}073 - 8669)\text{ kJ/kmol }N_2] \\ = {} & 363{,}880\text{ kJ/kmol of }C_3H_8 \end{aligned}$$

$$\dot{Q}_{\text{out}} = \dot{m}q_{\text{out}} = (0.05\text{ kg/min})(8270\text{ kJ/kg}) = 413.5\text{ kJ/min} = \mathbf{6.89\text{ kW}}$$

EXAMPLE 14–7

First-Law Analysis of Combustion in a Bomb

- The constant-volume tank shown contains 1 lbmol of methane (CH_4) gas and 3 lbmol of O_2 at 77°F and 1 atm. The contents of the tank are ignited, and the methane gas burns completely. If the final temperature is 1800 R, determine:
- (*a*) the final pressure in the tank and
- (*b*) the heat transfer during this process.



ADIABATIC FLAME TEMPERATURE

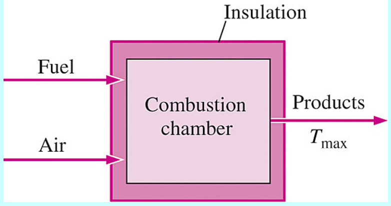
In the absence of any work interactions and any changes in kinetic or potential energies, the chemical energy released during a combustion process either is lost as heat to the surroundings or is used internally to raise the temperature of the combustion products.

The smaller the heat loss, the larger the temperature rise. In the limiting case of no heat loss to the surroundings (Q = 0), the temperature of the products reaches a maximum, which is called the **adiabatic flame** or **adiabatic combustion temperature** of the reaction (See Figure).

The adiabatic flame temperature of a steady-flow combustion process is determined from this Equation by setting $Q = 0$ and $W = 0$. It yields:

$$Q - W = H_{\text{prod}} - H_{\text{react}}$$

$$H_{\text{prod}} = H_{\text{react}}$$



ADIABATIC FLAME TEMPERATURE

Once the reactants and their states are specified, the enthalpy of the reactants H_{react} can be easily determined.

The calculation of the enthalpy of the products H_{prod} is not so straightforward, however, because the temperature of the products is not known prior to the calculations.

Therefore, the determination of the adiabatic flame temperature requires the use of an iterative technique unless equations for the sensible enthalpy changes of the combustion products are available.

A temperature is assumed for the product gases, and the H_{prod} is determined for this temperature. If it is not equal to H_{react}, calculations are repeated with another temperature. The adiabatic flame temperature is then determined from these two results by interpolation.

When the oxidant is air, the product gases mostly consist of N_2, and a good first guess for the adiabatic flame temperature is obtained by treating the entire product gases as N_2.

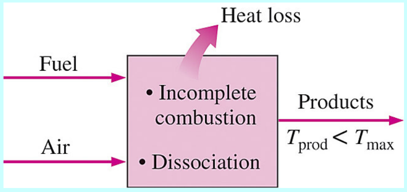
ADIABATIC FLAME TEMPERATURE

In combustion chambers, the highest temperature to which a material can be exposed is limited by metallurgical considerations.

Therefore, the adiabatic flame temperature is an important consideration in the design of combustion chambers, gas turbines, and nozzles.

The maximum temperatures that occur in these devices are considerably lower than the adiabatic flame temperature, however, since the combustion is usually incomplete, some heat loss takes place, and some combustion gases dissociate at high temperatures (See Figure).

Note that the adiabatic flame temperature depends on (1) the state of the reactants, (2) the degree of completion of the reaction, and (3) the amount of air used. For a specified fuel at a specified state burned with air at a specified state:



the adiabatic flame temperature attains (reaches) its maximum value when complete combustion occurs with the theoretical amount of air.

EXAMPLE 14–8

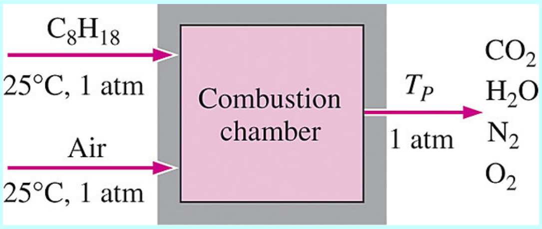
Adiabatic Flame Temperature in Steady Combustion

- Liquid octane (C_8H_{18}) enters the combustion chamber of a gas turbine steadily at 1 atm and 25°C, and it is burned with air that enters the combustion chamber at the same state, as shown. Determine the adiabatic flame temperature for
- (*a*) complete combustion with 100 percent theoretical air,
- (*b*) complete combustion with 400 percent theoretical air, and
- (*c*) incomplete combustion (some CO in the products) with 90 percent theoretical air.

(a) $T_{\text{prod}} = 2395\ \text{K}$

(b) $T_{\text{prod}} = 962\ \text{K}$

(c) $T_{\text{prod}} = 2236\ \text{K}$



ENTROPY CHANGE OF REACTING SYSTEMS

The entropy balance relation can be expressed more explicitly for a *closed* or *steady-flow* reacting system as:

$$\sum \frac{Q_k}{T_k} + S_{\text{gen}} = S_{\text{prod}} - S_{\text{react}}$$

For an *adiabatic process* ($Q = 0$), the entropy transfer term drops out and this Equation reduces to:

$$S_{\text{gen,adiabatic}} = S_{\text{prod}} - S_{\text{react}} \geq 0$$

The determination of the entropy change associated with a chemical reaction seems to be straightforward, except for one thing:

The entropy relations for the reactants and the products involve the *entropies* of the components, *not entropy changes*, which was the case for non-reacting systems.

Thus we are faced with the problem of finding a common base for the entropy of all substances, as we did with enthalpy.

ENTROPY CHANGE OF REACTING SYSTEMS

The search for such a common base led to the establishment of the **THIRD LAW OF THERMODYNAMICS** in the early part of this century.

The third law was expressed in previous chapter as follows: *The entropy of a pure crystalline substance at absolute zero temperature is zero*.

Entropy values relative to this base are called the **absolute entropy.**

The $s°$ values listed in Tables A–18 through A–25 for various gases such as N_2, O_2, CO, CO_2 , H_2, H_2O, OH, and O are the *ideal-gas absolute entropy values* at the specified temperature and *at a pressure of 1 atm*.

The absolute entropy values for various fuels are listed in Table A–26 together with the $h°f$ values at the standard reference state of 25°C and 1 atm.

The equation above requires the determination of the entropy of each individual component of the reactants and the products, which in general is not very easy to do.

ENTROPY CHANGE OF REACTING SYSTEMS

The entropy calculations can be simplified somewhat if the gaseous components of the reactants and the products are approximated as ideal gases.

However, entropy calculations are never as easy as enthalpy or internal energy calculations, since entropy is a function of both temperature and pressure even for ideal gases.

When evaluating the entropy of a component of an ideal-gas mixture, we should use the temperature and the partial pressure of the component.

Note that the temperature of a component is the same as the temperature of the mixture, and the partial pressure of a component is equal to the mixture pressure multiplied by the mole fraction of the component.

$$\bar{s}_i(T,P_i) = \bar{s}_i^\circ(T,P_0) - R_u \ln \frac{y_i P_m}{P_0}$$

SECOND-LAW ANALYSIS OF REACTING SYSTEMS

Once the total entropy change or the entropy generation is evaluated, the **exergy destroyed** $X_{\text{destroyed}}$ associated with a chemical reaction can be determined from:

$$X_{\text{destroyed}} = T_0 S_{\text{gen}}$$

the reversible work relation for a steady-flow combustion process that involves heat transfer with only the surroundings at T_0 can be obtained by replacing the enthalpy terms h by:

$$\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ$$

yielding:

$$W_{\text{rev}} = \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0\bar{s})_r - \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - T_0\bar{s})_p$$

EXAMPLE 14–10

Second-Law Analysis of Adiabatic Combustion

- Methane (CH_4) gas enters a steady-flow adiabatic combustion chamber at 25°C and 1 atm. It is burned with 50 percent excess air that also enters at 25°C and 1 atm, as shown. Assuming complete combustion, determine:
- (*a*) the temperature of the products,
- (*b*) the entropy generation, and
- (*c*) the reversible work and exergy destruction.
- Assume that T_0 298 K and the products leave the combustion chamber at 1 atm pressure.