Chapter 3
FUELS AND COMBUSTION

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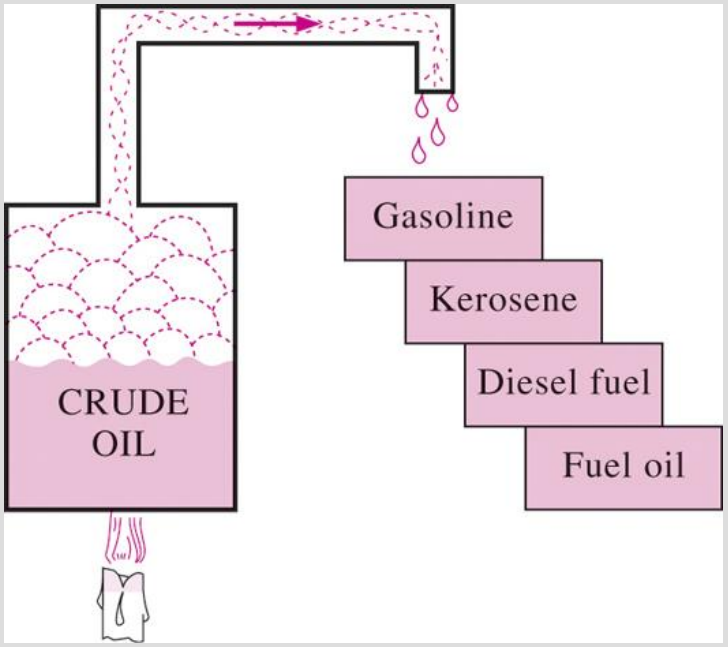
FUELS AND COMBUSTION

Fuel: Any material that can be burned to release thermal energy.

Most familiar fuels consist primarily of hydrogen and carbon.

They are called **hydrocarbon fuels** and are denoted by the general formula C_nH_m.

Hydrocarbon fuels exist in all phases, some examples being coal, gasoline (usually treated as octane C_8H_{18}), and natural gas.



Most liquid hydrocarbon fuels are obtained from crude oil by distillation.

TABLE 15–1

A comparison of some alternative fuels to the traditional petroleum-based fuels used in transportation

Fuel	Energy content kJ/L	Gasoline equivalence,* L/L-gasoline
Gasoline	31,850	1
Light diesel	33,170	0.96
Heavy diesel	35,800	0.89
LPG (Liquefied petroleum gas, primarily propane)	23,410	1.36
Ethanol (or ethyl alcohol)	29,420	1.08
Methanol (or methyl alcohol)	18,210	1.75
CNG (Compressed natural gas, primarily methane, at 200 atm)	8,080	3.94
LNG (Liquefied natural gas, primarily methane)	20,490	1.55

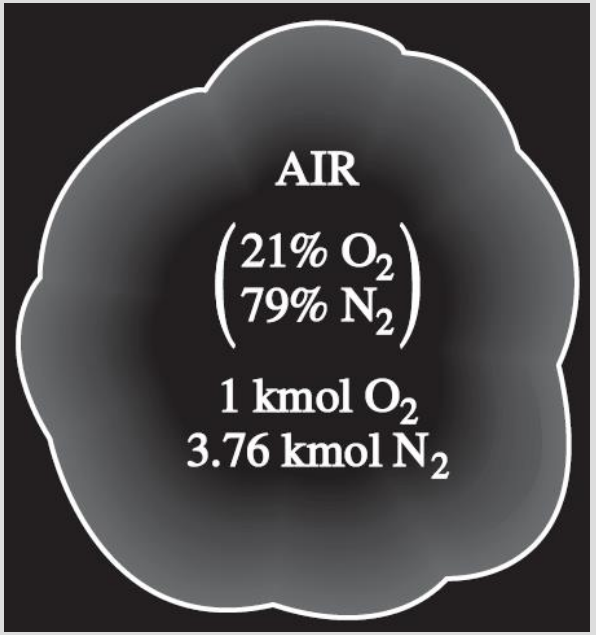
**Amount of fuel whose energy content is equal to the energy content of 1-L gasoline.*

The oxidizer most often used in combustion processes is air. Why?

On a mole or a volume basis, dry air is composed of 20.9% O_2, 78.1% N_2, 0.9% Ar, and small amounts of CO_2, He, Ne, H_2.

In the analysis of combustion processes, dry air is approximated as 21% O_2 and 79% N_2 by mole numbers.

$$1\ \text{kmol}\ O_2 + 3.76\ \text{kmol}\ N_2 = 4.76\ \text{kmol air}$$

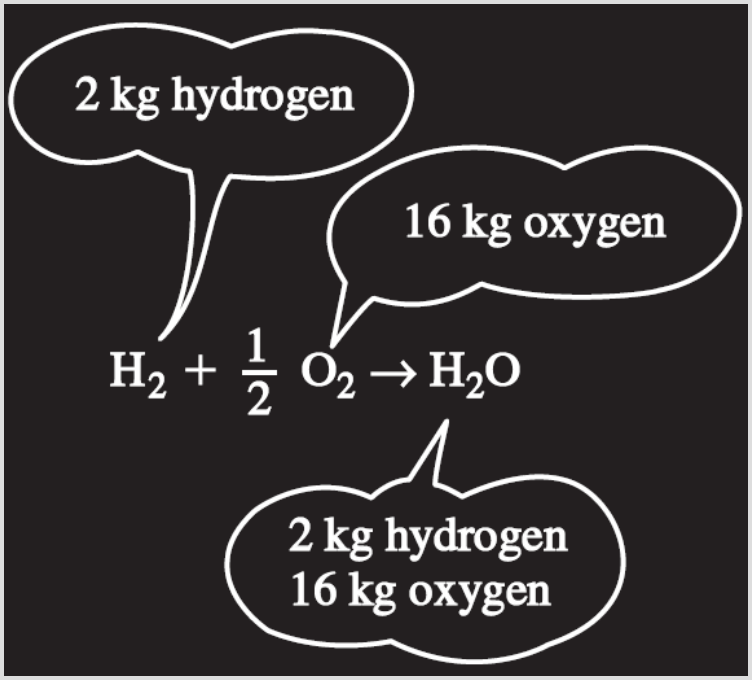


Each kmol of O_2 in air is accompanied by 3.76 kmol of N_2.

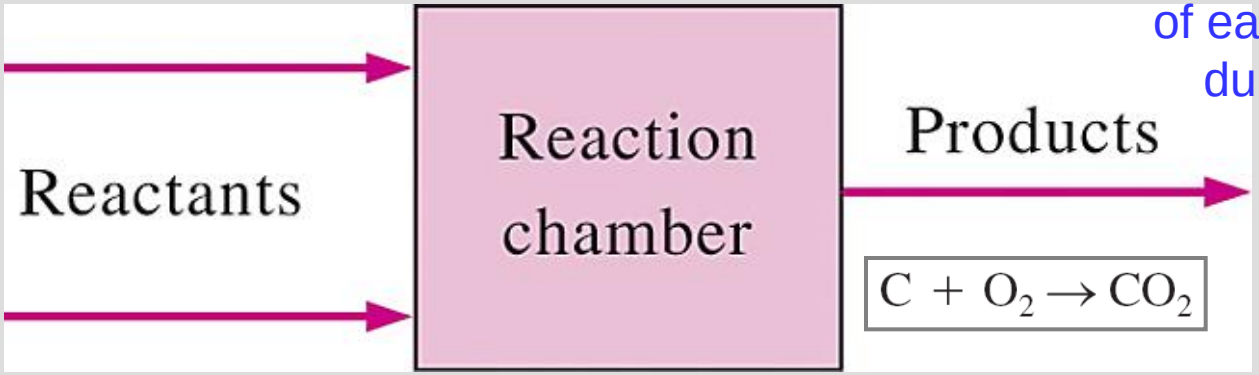
Combustion is a chemical reaction during which a fuel is oxidized and a large quantity of energy is released.

The fuel must be brought above its **ignition temperature** to start the combustion. The minimum ignition temperatures in atmospheric air are approximately 260°C for gasoline, 400°C for carbon, 580°C for hydrogen, 610°C for carbon monoxide, and 630°C for methane.

Proportions of the fuel and air must be in the proper range for combustion to begin. For example, natural gas does not burn in air in concentrations less than 5% or greater than about 15%.



The mass (and number of atoms) of each element is conserved during a chemical reaction.



The total number of moles is not conserved during a chemical reaction.

In a steady-flow combustion process, the components that enter the reaction chamber are called reactants and the components that exit are called products.

Air-fuel ratio (AF) is usually expressed on a mass basis and is defined as *the ratio of the mass of air to the mass of fuel* for a combustion process

$$AF = \frac{m_{air}}{m_{fuel}}$$

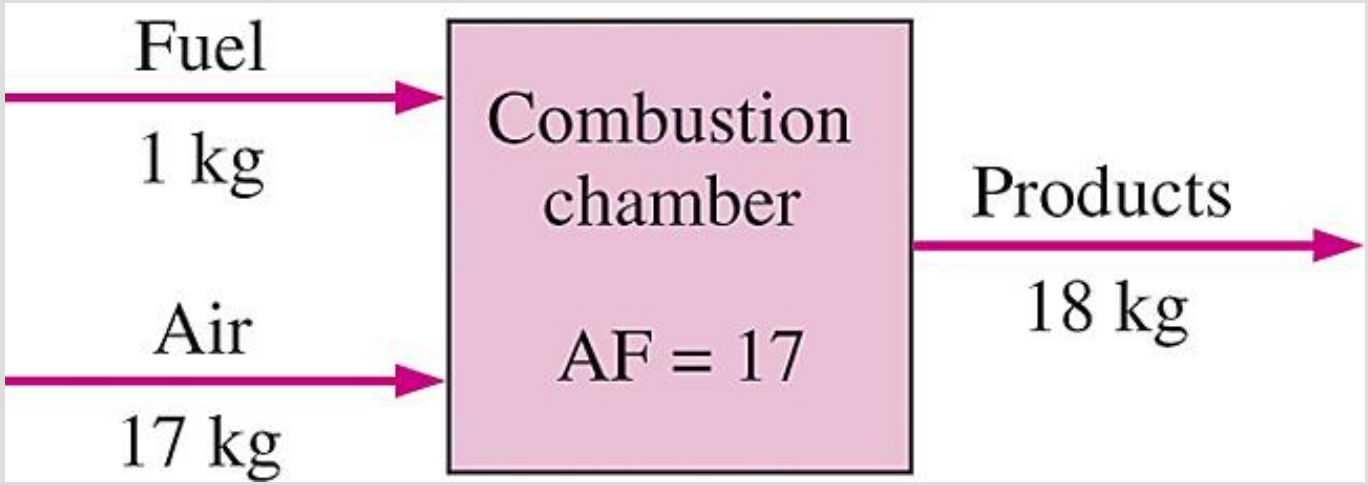
$m = NM$

m mass

N number of moles

M molar mass

Fuel–air ratio (FA): The reciprocal of air–fuel ratio.



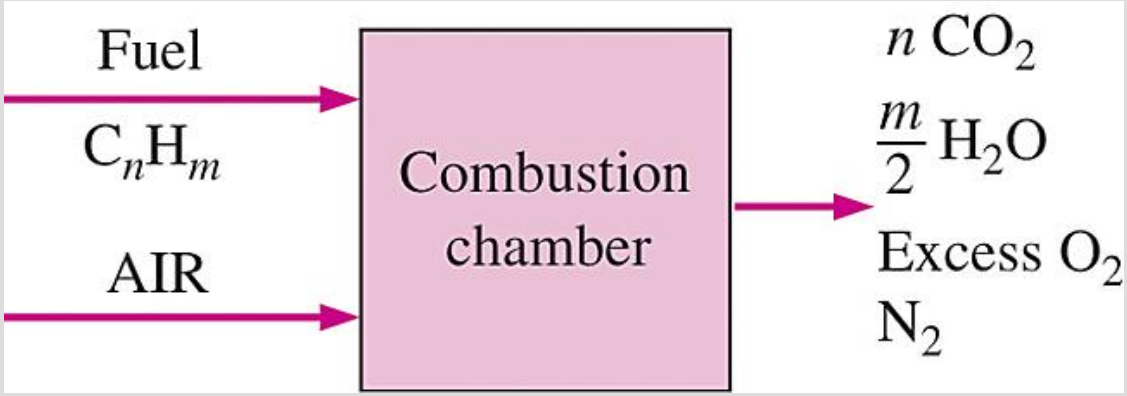
The air–fuel ratio (AF) represents the amount of air used per unit mass of fuel during a combustion process.

THEORETICAL AND ACTUAL COMBUSTION PROCESSES

Complete combustion: If all the carbon in the fuel burns to CO_2, all the hydrogen burns to H_2O, and all the sulfur (if any) burns to SO_2.

Incomplete combustion: If the combustion products contain any unburned fuel or components such as C, H_2, CO, or OH.

Reasons for incomplete combustion: 1 ***Insufficient oxygen***, **2** ***insufficient mixing*** in the combustion chamber during the limited time that the fuel and the oxygen are in contact, and **3** ***dissociation*** (at high temperatures).



A combustion process is complete if all the combustible components of the fuel are burned to completion.

Oxygen has a much greater tendency to combine with hydrogen than it does with carbon. Therefore, the hydrogen in the fuel normally burns to completion, forming H_2O.

Stoichiometric or **theoretical air:** The minimum amount of air needed for the complete combustion of a fuel. Also referred to as the *chemically correct amount of air,* or *100% theoretical air.*

Stoichiometric or **theoretical combustion:** The ideal combustion process during which a fuel is burned completely with theoretical air.

Excess air: The amount of air in excess of the stoichiometric amount. Usually expressed in terms of the stoichiometric air as *percent excess air* or *percent theoretical air.*

Deficiency of air: Amounts of air less than the stoichiometric amount. Often expressed as *percent deficiency of air.*

Equivalence ratio: The ratio of the actual fuel–air ratio to the stoichiometric fuel–air ratio.

50% excess air = 150% theoretical air
200% excess air = 300% theoretical air.
90% theoretical air = 10% deficiency of air

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$$

- no unburned fuel
- no free oxygen in products

The complete combustion process with no free oxygen in the products is called theoretical combustion.

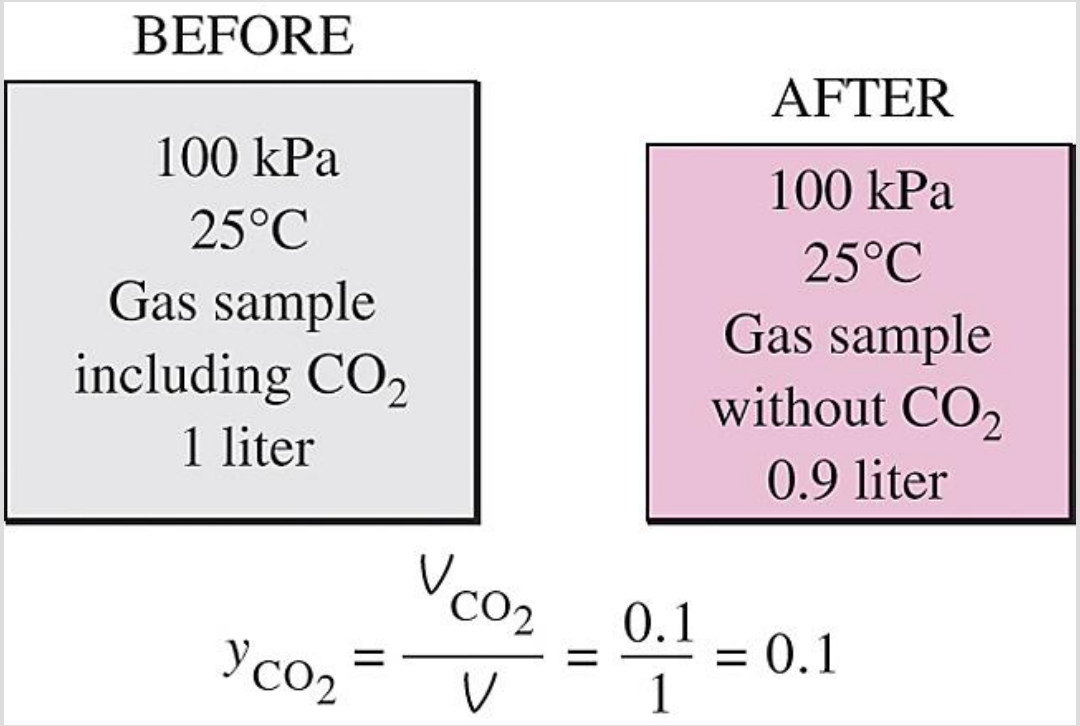
Predicting the composition of the products is relatively easy when the combustion process is assumed to be complete.

With actual combustion processes, it is impossible to predict the composition of the products on the basis of the mass balance alone.

Then the only alternative we have is to measure the amount of each component in the products directly.

A commonly used device to analyze the composition of combustion gases is the **Orsat gas analyzer**.

The results are reported on a dry basis.

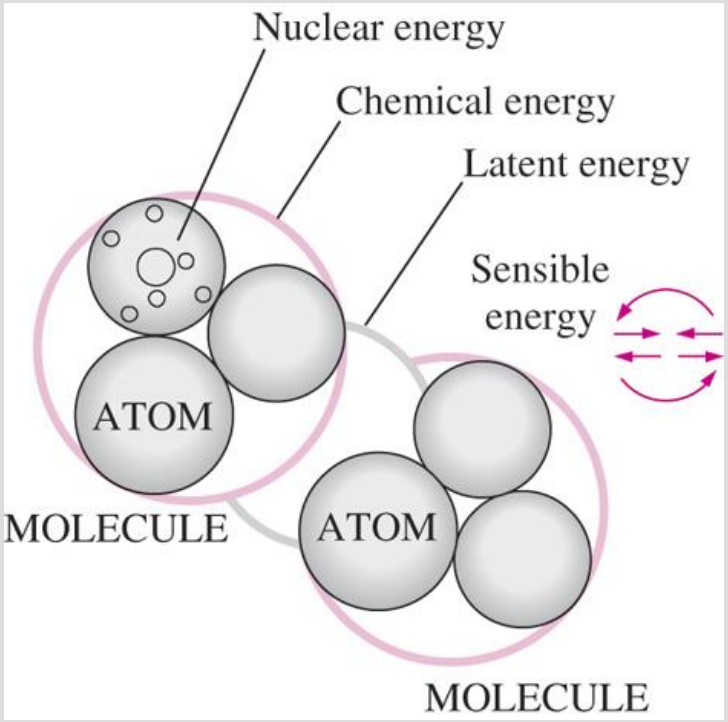


Determining the mole fraction of the CO_2 in combustion gases by using the Orsat gas analyzer.

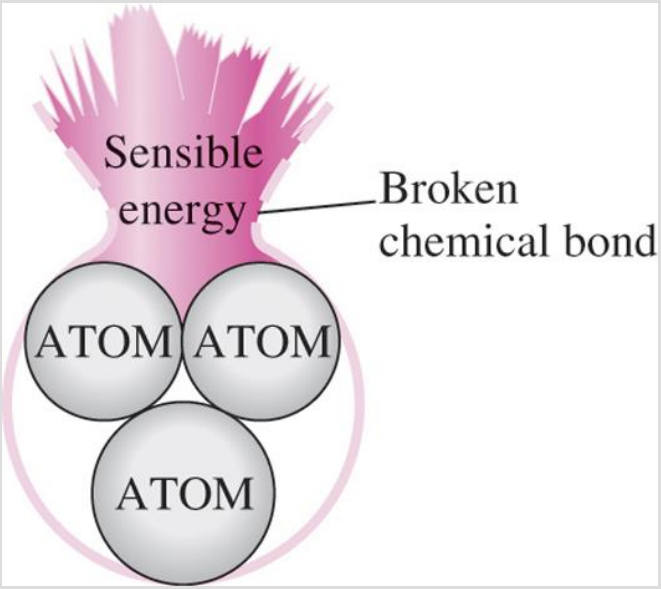
ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

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:

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



The microscopic form of energy of a substance consists of sensible, latent, chemical, and nuclear energies.



When the existing chemical bonds are destroyed and new ones are formed during a combustion process, usually a large amount of sensible energy is absorbed or released.

Enthalpy of reaction h_R : 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.

Enthalpy of combustion h_C : It is the enthalpy of reaction for combustion processes. It 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.

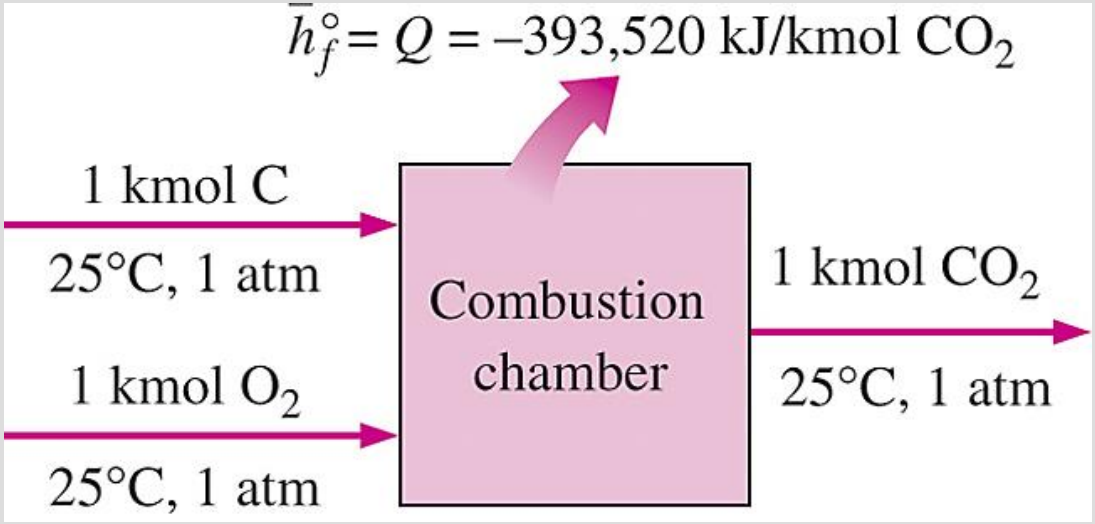
The enthalpy of formation h_f : The amount of energy absorbed or released as the component is formed from its stable elements during a steady-flow process at a specified state.

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

$$\bar{h}_C = Q = -393{,}520 \text{ kJ/kmol C}$$

$$\bar{h}_f^\circ = Q = -393{,}520 \text{ kJ/kmol } CO_2$$

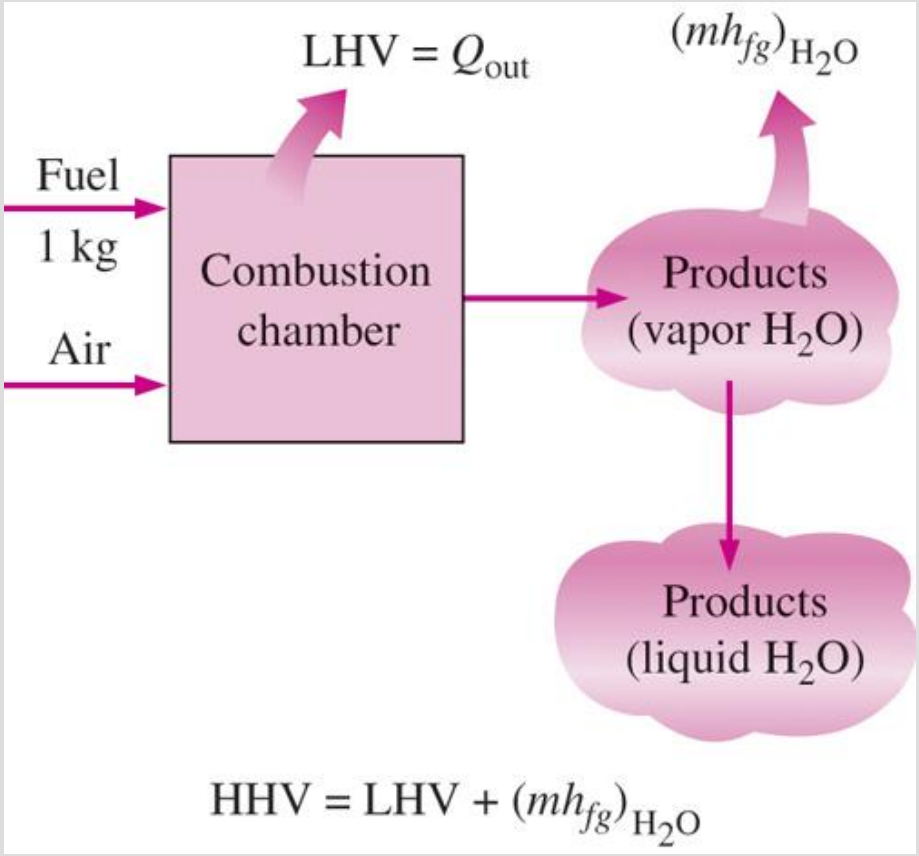
To establish a starting point, we assign the enthalpy of formation of all stable elements (such as O_2, N_2, H_2, and C) a value of zero at the standard reference state of 25°C and 1 atm.



Heating value: 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. The heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel.

Higher heating value (HHV): When the H_2O in the products is in the liquid form.

Lower heating value (LHV): When the H_2O in the products is in the vapor form.



The higher heating value of a fuel is equal to the sum of the lower heating value of the fuel and the latent heat of vaporization of the H_2O in the products.

$$\text{Heating value} = |h_C| \qquad (\text{kJ/kg fuel})$$

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

For the fuels with variable composition (i.e., coal, natural gas, fuel oil), the heating value may be determined by burning them directly in a **bomb calorimeter**.

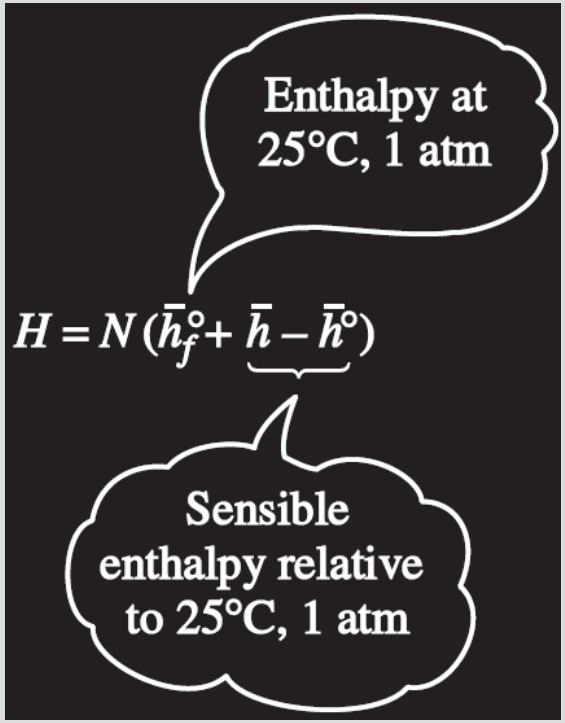
FIRST-LAW ANALYSIS OF REACTING SYSTEMS

The energy balance (the first-law) relations developed in Chaps. 4 and 5 are applicable to both reacting and nonreacting systems. We rewrite the energy balance relations including the changes in chemical energies.

Steady-Flow Systems

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

When the changes in kinetic and potential energies are negligible, the steady-flow energy balance for a *chemically reacting steady-flow system:*



The enthalpy of a chemical component at a specified state

$$\dot{E}_{\text{in}} = \dot{E}_{\text{out}}$$

$$\underbrace{\dot{Q}_{\text{in}} + \dot{W}_{\text{in}} + \sum \dot{n}_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r}_{\text{Rate of net energy transfer in by heat, work, and mass}} = \underbrace{\dot{Q}_{\text{out}} + \dot{W}_{\text{out}} + \sum \dot{n}_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p}_{\text{Rate of net energy transfer out by heat, work, and mass}}$$

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

Taking heat transfer *to* the system and work done *by* the system to be *positive* quantities, the energy balance relation is

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

or as

$$Q - W = H_{\text{prod}} - H_{\text{react}} \qquad \text{(kJ/kmol fuel)}$$

where

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

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

If the enthalpy of combustion for a particular reaction is available:

$$Q - W = \bar{h}_C^\circ + \sum N_p(\bar{h} - \bar{h}^\circ)_p - \sum N_r(\bar{h} - \bar{h}^\circ)_r \qquad \text{(kJ/kmol)}$$

Most steady-flow combustion processes do not involve any work interactions. Also, combustion chamber normally involves heat output but no heat input:

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

Closed Systems

Taking heat transfer *to* the system and work done *by* the system to be *positive* quantities, the general closed-system energy balance relation can be expressed for a stationary *chemically reacting closed system* as

$$E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$$

$$(Q_{\text{in}} - Q_{\text{out}}) + (W_{\text{in}} - W_{\text{out}}) = U_{\text{prod}} - U_{\text{react}} \qquad (\text{kJ/kmol fuel})$$

$$\begin{aligned} U &= H - PV \\ &= N(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ) - PV \\ &= N(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v}) \end{aligned}$$

An expression for the internal energy of a chemical component in terms of the enthalpy.

Utilizing the definition of enthalpy:

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

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

The *Pv* terms are negligible for solids and liquids, and can be replaced by $R_u T$ for gases that behave as an ideal gas.

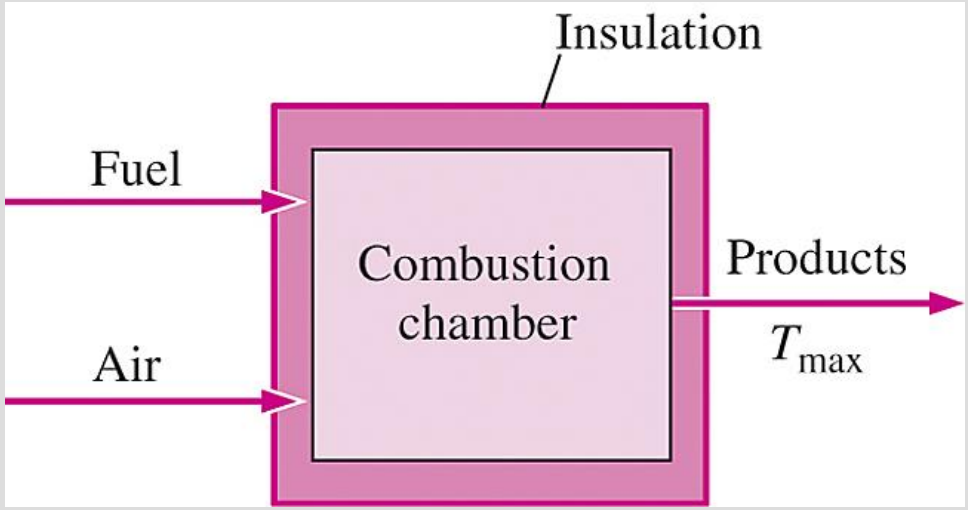
ADIABATIC FLAME TEMPERATURE

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.**

$$H_{prod} = H_{react} \quad \text{since} \quad Q = 0 \text{ and } W = 0$$

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

The determination of the adiabatic flame temperature by hand requires the use of an iterative technique.



The temperature of a combustion chamber becomes maximum when combustion is complete and no heat is lost to the surroundings ($Q = 0$).

EXAMPLE 15–5 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.

Solution The enthalpy of combustion of a fuel is to be determined using enthalpy of formation data.

Properties The enthalpy of formation at 25°C and 1 atm is −393,520 kJ/kmol for CO_2, −285,830 kJ/kmol for $H_2O(\ell)$, and −249,950 kJ/kmol for $C_8H_{18}(\ell)$ (Table A–26).

Analysis The combustion of C_8H_{18} is illustrated in Fig. 15–20. The stoichiometric equation for this reaction is

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

Both the reactants and the products are at the standard reference state of 25°C and 1 atm. Also, N_2 and O_2 are stable elements, and thus their enthalpy of formation is zero. Then the enthalpy of combustion of C_8H_{18} becomes (Eq. 15–6)

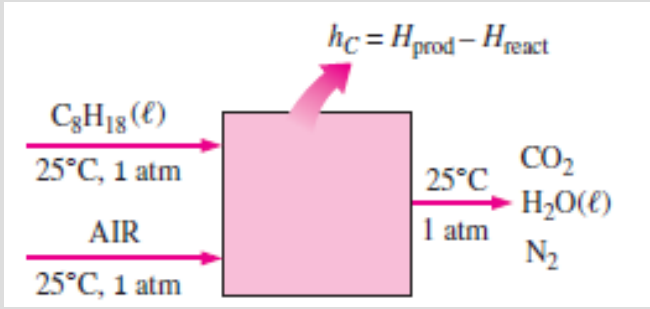
$$\bar{h}_C = H_{prod} - H_{react}$$
$$= \sum N_p \bar{h}^\circ_{f,p} - \sum N_r \bar{h}^\circ_{f,r} = (N\bar{h}^\circ_f)_{CO_2} + (N\bar{h}^\circ_f)_{H_2O} - (N\bar{h}^\circ_f)_{C_8H_{18}}$$

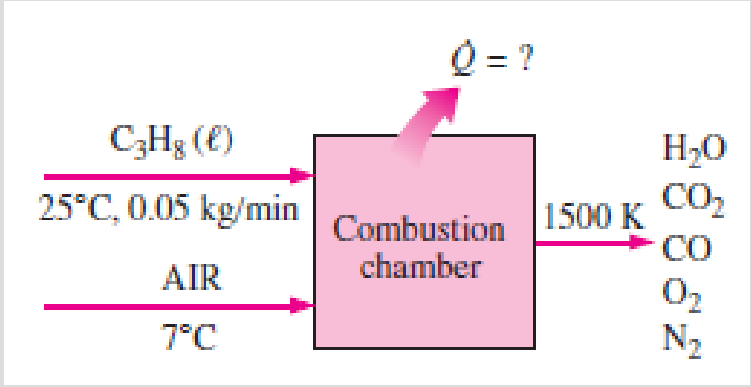
Substituting,

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

which is practially identical to the listed value of 47,890 kJ/kg in Table A–27. Since the water in the products is assumed to be in the liquid phase, this h_C value corresponds to the HHV of liquid C_8H_{18}.

Discussion It can be shown that the result for gaseous octane is −5,512,200 kJ/kmol or −48,255 kJ/kg.





EXAMPLE 15–6 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 in Fig. 15–23. 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 is 1500 K, determine (*a*) the mass flow rate of air and (*b*) the rate of heat transfer from the combustion chamber.

Solution Liquid propane is burned steadily with excess air. The mass flow rate of air and the rate of heat transfer are to be determined.

Assumptions **1** Steady operating conditions exist. **2** Air and the combustion gases are ideal gases. **3** Kinetic and potential energies are negligible.

Analysis We note that all the hydrogen in the fuel burns to H_2O but 10 percent of the carbon burns incompletely and forms CO. Also, the fuel is burned with excess air and thus there is some free O_2 in the product gases.

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 balance: $a_{th} = 3 + 2 = 5$

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 air–fuel ratio for this combustion process is

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

Thus,

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

(*b*) The heat transfer for this steady-flow combustion process is determined from the steady-flow energy balance $E_{out} = E_{in}$ applied on the combustion chamber per unit mole of the fuel,

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

or

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

Assuming the air and the combustion products to be ideal gases, we have $h = h(T)$, and we form the following minitable using data from the property tables:

Substance	$\bar{h}_f^\circ$ kJ/kmol	$\bar{h}_{280\ K}$ kJ/kmol	$\bar{h}_{298\ K}$ kJ/kmol	$\bar{h}_{1500\ K}$ 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

The $\bar{h}_f^\circ$ of liquid propane is obtained by subtracting the $\bar{h}_{fg}$ of propane at 25°C from the $\bar{h}_f^\circ$ of gas propane. Substituting gives

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

Thus 363,880 kJ of heat is transferred from the combustion chamber for each kmol (44 kg) of propane. This corresponds to 363,880/44 = 8270 kJ of heat loss per kilogram of propane. Then the rate of heat transfer for a mass flow rate of 0.05 kg/min for the propane becomes

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

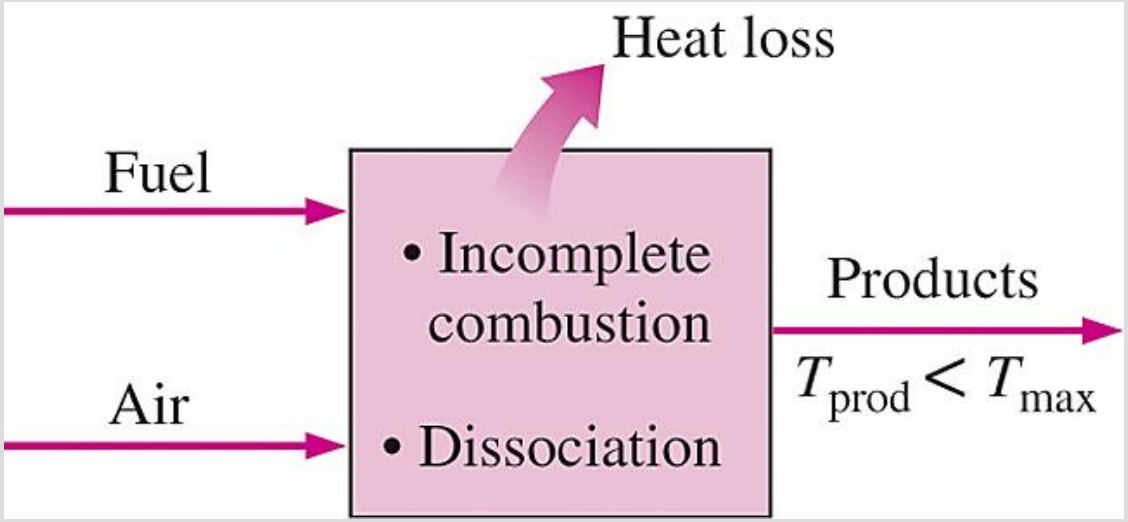
The adiabatic flame temperature of a fuel depends on

(1) the state of the reactants

(2) the degree of completion of the reaction

(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 its maximum value when complete combustion occurs with the theoretical amount of air.*



The maximum temperature encountered in a combustion chamber is lower than the theoretical adiabatic flame temperature.

ENTROPY CHANGE OF REACTING SYSTEMS

$$\underbrace{S_{in} - S_{out}}_{\text{Net entropy transfer by heat and mass}} + \underbrace{S_{gen}}_{\text{Entropy generation}} = \underbrace{\Delta S_{system}}_{\text{Change in entropy}} \quad (\text{kJ/K})$$

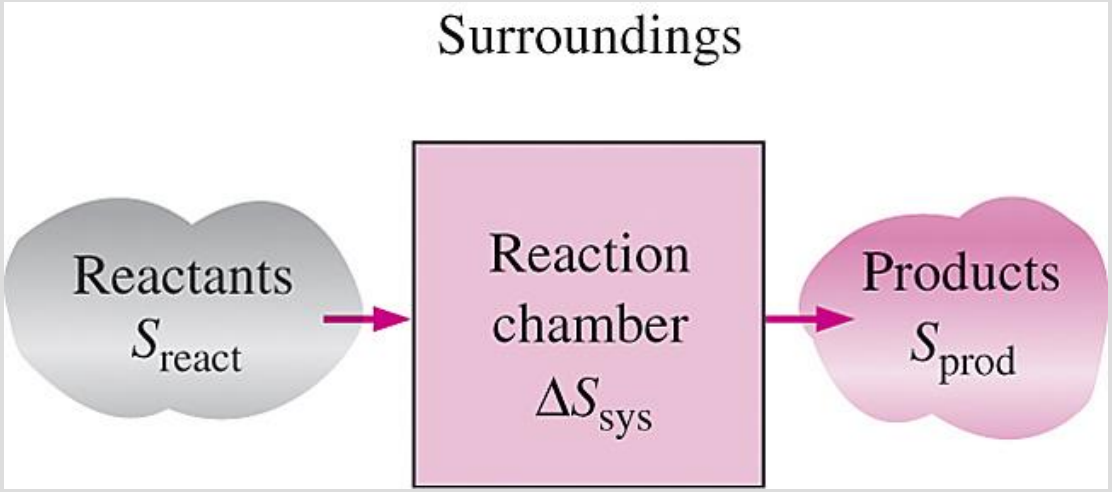
entropy balance for *any system* (including reacting systems) undergoing *any process*

$$\sum \frac{Q_k}{T_k} + S_{gen} = S_{prod} - S_{react} \quad (\text{kJ/K})$$

for a *closed* or *steady-flow* reacting system

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

for an *adiabatic process* ($Q = 0$)



The entropy change associated with a chemical relation.

SECOND-LAW ANALYSIS OF REACTING SYSTEMS

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} \qquad (\text{kJ})$$

Exergy destruction

The reversible work for a steady-flow combustion process that involves heat transfer with only the surroundings at T_0

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