Chapter 15
CHEMICAL REACTIONS

Objectives

- Give an overview of fuels and combustion.

- Apply the conservation of mass to reacting systems to determine balanced reaction equations.

- Define the parameters used in combustion analysis, such as air–fuel ratio, percent theoretical air, and dew-point temperature.

- Apply energy balances to reacting systems for both steady-flow control volumes and fixed mass systems.

- Calculate the enthalpy of reaction, enthalpy of combustion, and the heating values of fuels.

- Determine the adiabatic flame temperature for reacting mixtures.

- Evaluate the entropy change of reacting systems.

- Analyze reacting systems from the second-law perspective.
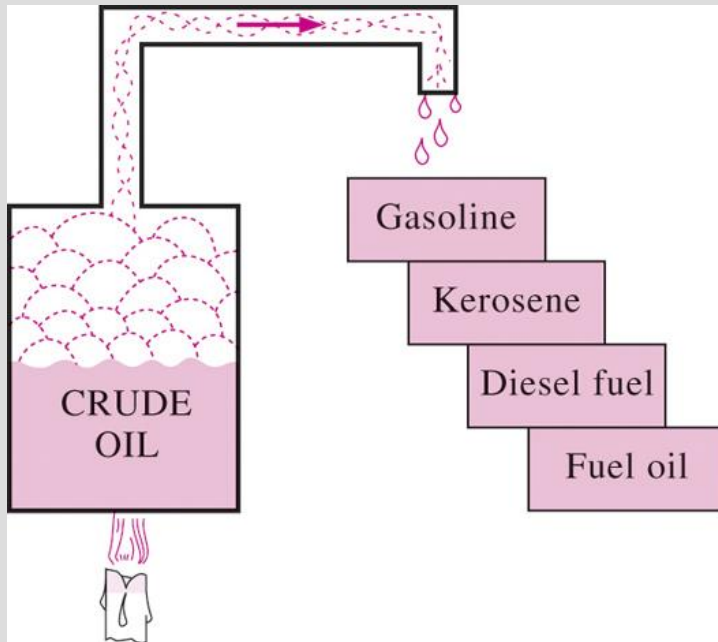
FUELS AND COMBUSTION

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.

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

AIR

$$\begin{pmatrix} 21\% \ O_2 \\ 79\% \ N_2 \end{pmatrix}$$

1 kmol O_2
3.76 kmol N_2
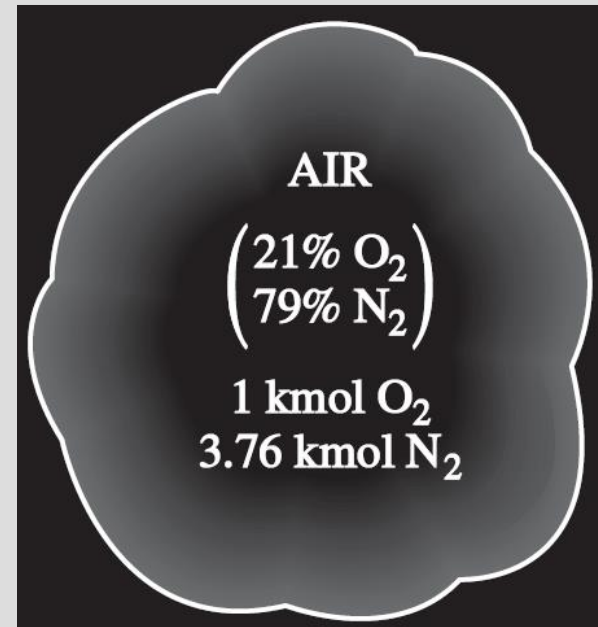
Combustion is a chemical reaction during which a fuel is oxidized and a large quantity of energy is released.
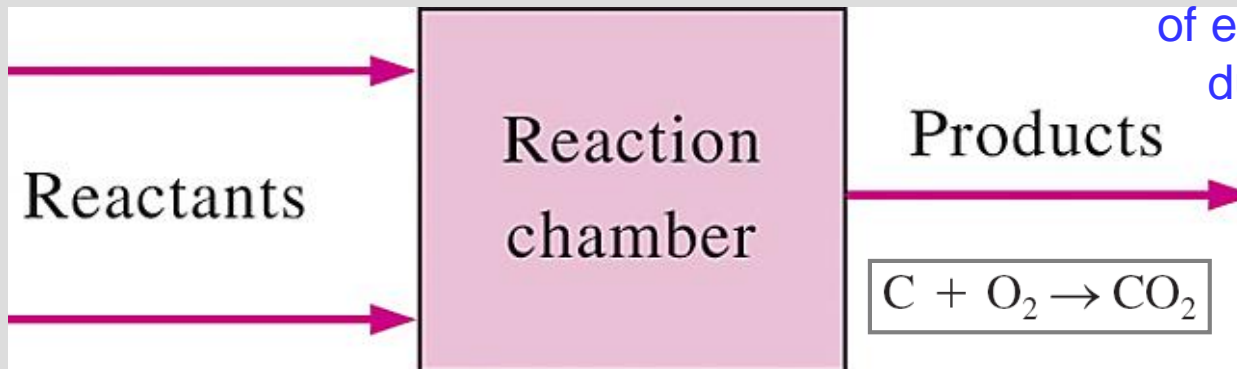
Each kmol of O_2 in air is accompanied by 3.76 kmol of N_2.

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%.

2 kg hydrogen

16 kg oxygen

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

2 kg hydrogen
16 kg oxygen
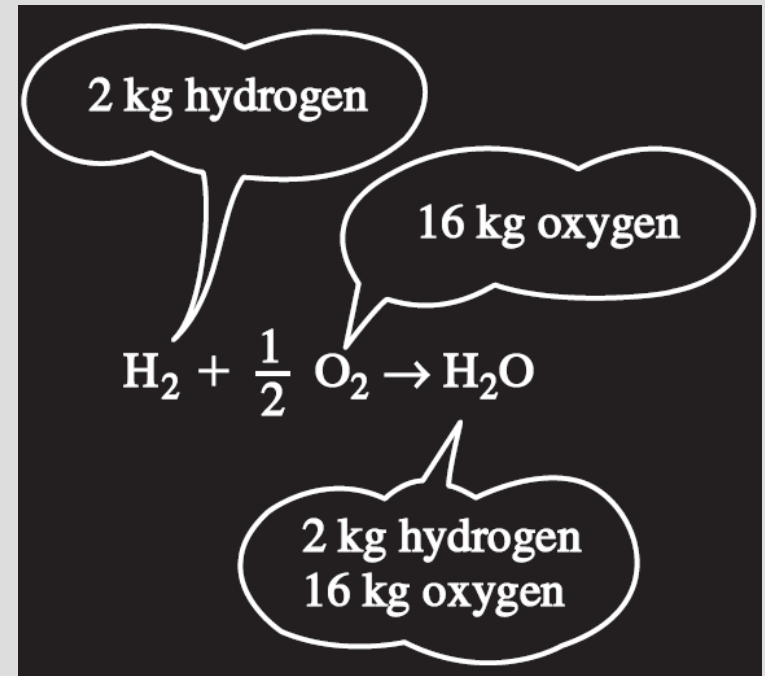
The mass (and number of atoms) of each element is conserved during a chemical reaction.

Reactants

Reaction chamber

Products

$$C + O_2 \rightarrow CO_2$$

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

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

$$m = NM$$

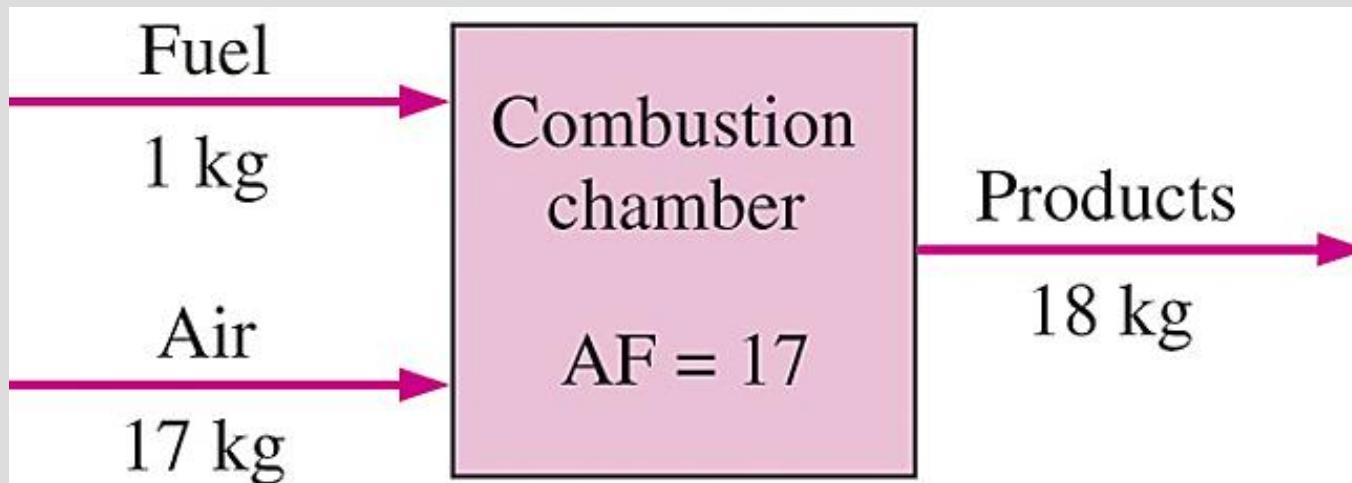*m* mass

N number of moles

M molar mass

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

Fuel
1 kg

Air
17 kg

Combustion chamber

AF = 17

Products
18 kg

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).

Fuel

C_nH_m

AIR

Combustion chamber

$n \, CO_2$

$\frac{m}{2} \, H_2O$

Excess O_2

N_2
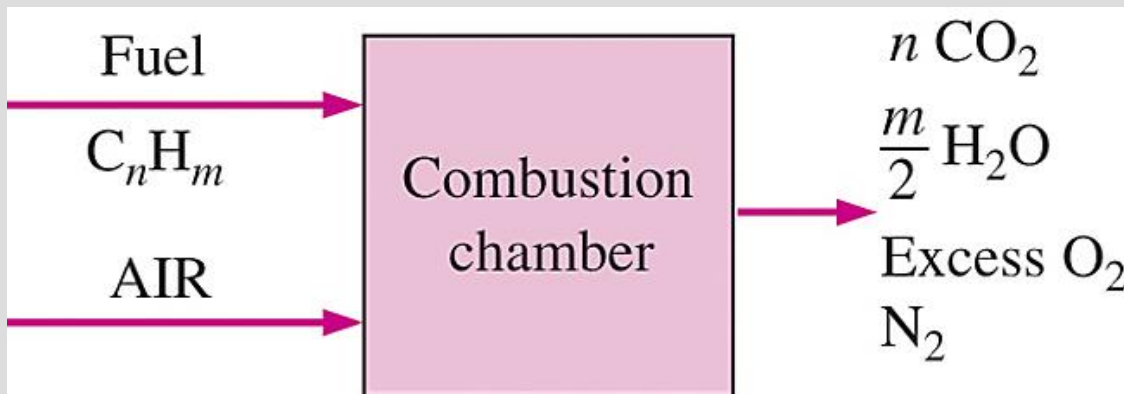
A combustion process is complete if all the combustible components of the fuel are burned to completion.

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

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow$$
$$CO_2 + 2H_2O + 7.52N_2$$
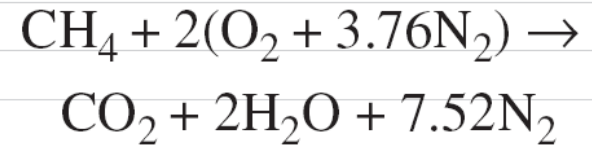
• no unburned fuel

• 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.

BEFORE

100 kPa
25°C
Gas sample
including CO_2
1 liter

AFTER

100 kPa
25°C
Gas sample
without CO_2
0.9 liter
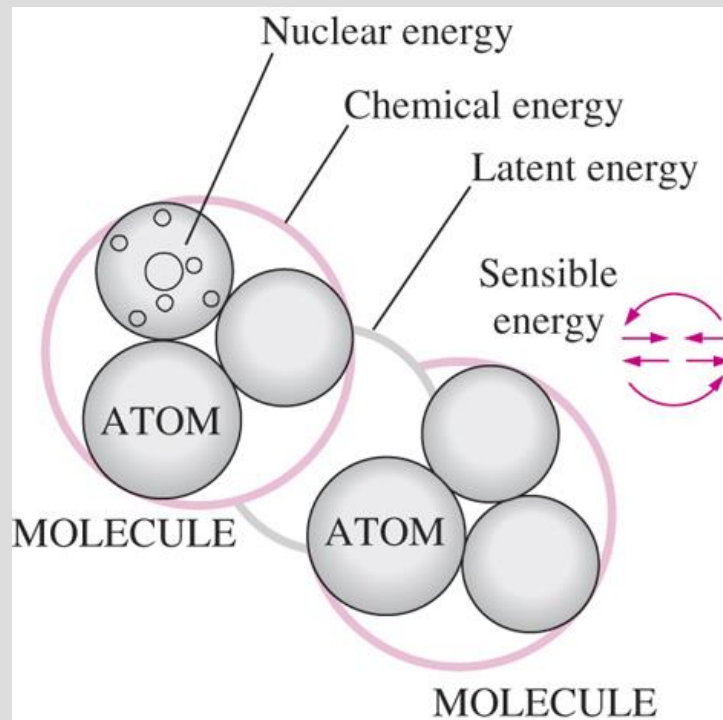
$$y_{CO_2} = \frac{V_{CO_2}}{V} = \frac{0.1}{1} = 0.1$$

Determining the mole fraction of the CO_2 in combustion gases by using the Orsat gas analyzer.
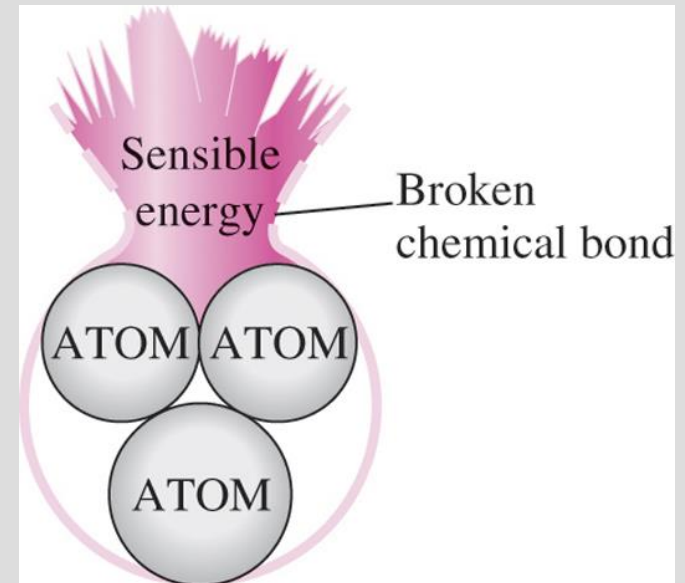
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ENTHALPY OF FORMATION AND ENTHALPY OF COMBUSTION

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.

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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.

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

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

$$\overline{h}_f^{\circ} = Q = -393{,}520 \text{ kJ/kmol CO}_2$$

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.

1 kmol C
25°C, 1 atm

1 kmol O_2
25°C, 1 atm

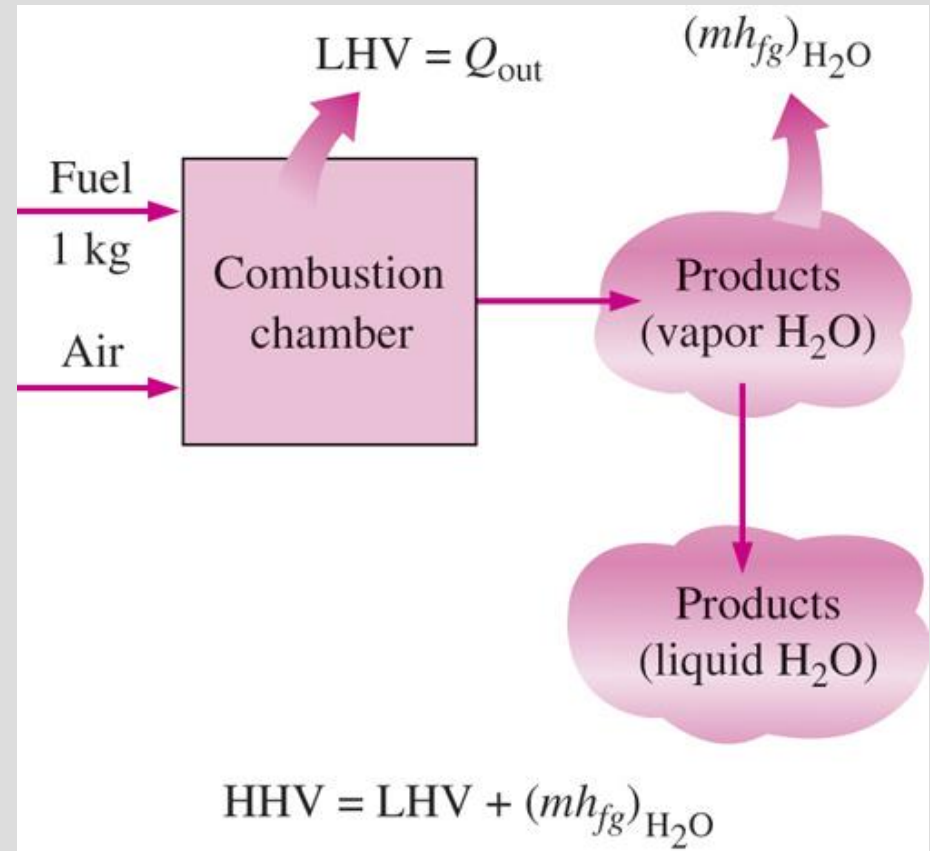Combustion chamber

1 kmol CO_2
25°C, 1 atm
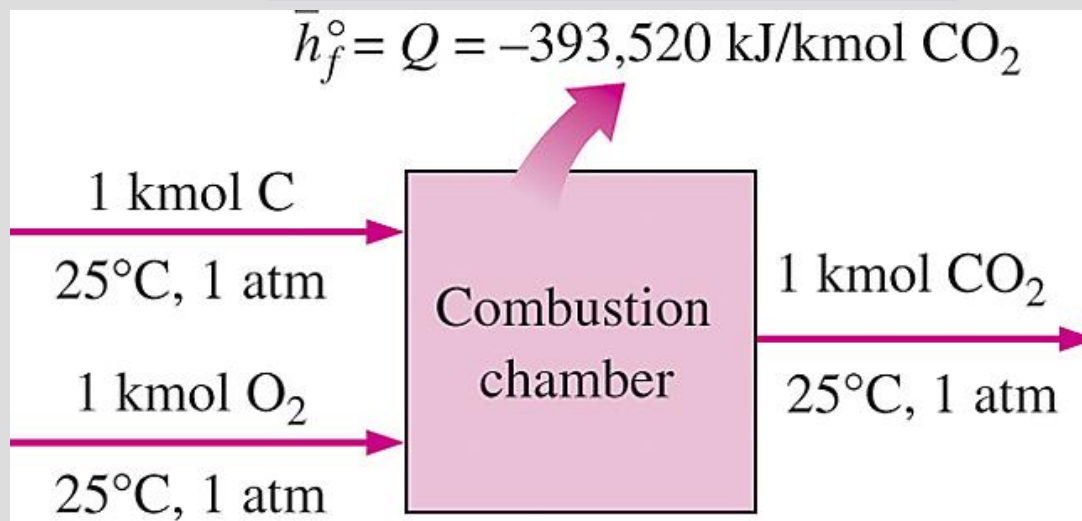
Heating value: The amount of heat released when a fuel is burned completely in a steady-flow process and the products are returned to the state of the reactants. The heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel.

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.

$$LHV = Q_{out}$$

$$(mh_{fg})_{H_2O}$$

Fuel 1 kg → Combustion chamber → Products (vapor H_2O)

Air →

Products (liquid H_2O)

$$HHV = LHV + (mh_{fg})_{H_2O}$$

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.

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

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

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**.

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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.
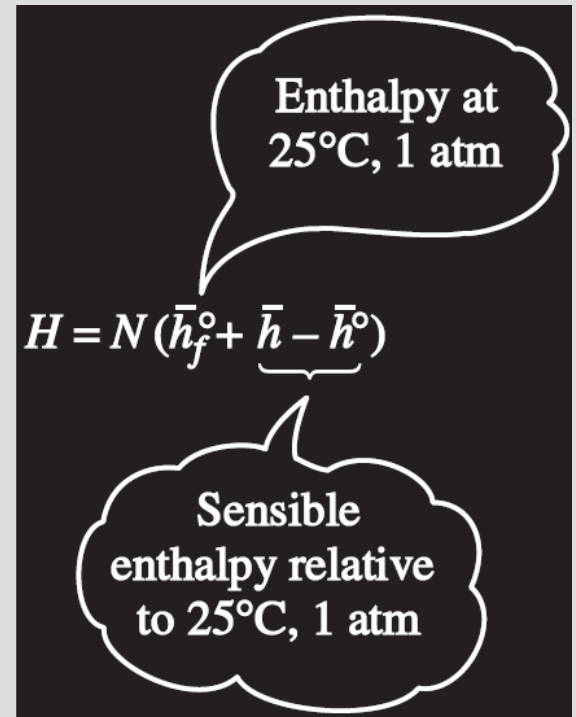
Steady-Flow Systems

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

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

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

Enthalpy at 25°C, 1 atm

$$H = N(\bar{h}_f^\circ + \underbrace{\bar{h} - \bar{h}^\circ})$$

Sensible enthalpy relative to 25°C, 1 atm

The enthalpy of a chemical component at a specified state

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

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

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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:

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

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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

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

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

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

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

Utilizing the definition of enthalpy:

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

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

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.
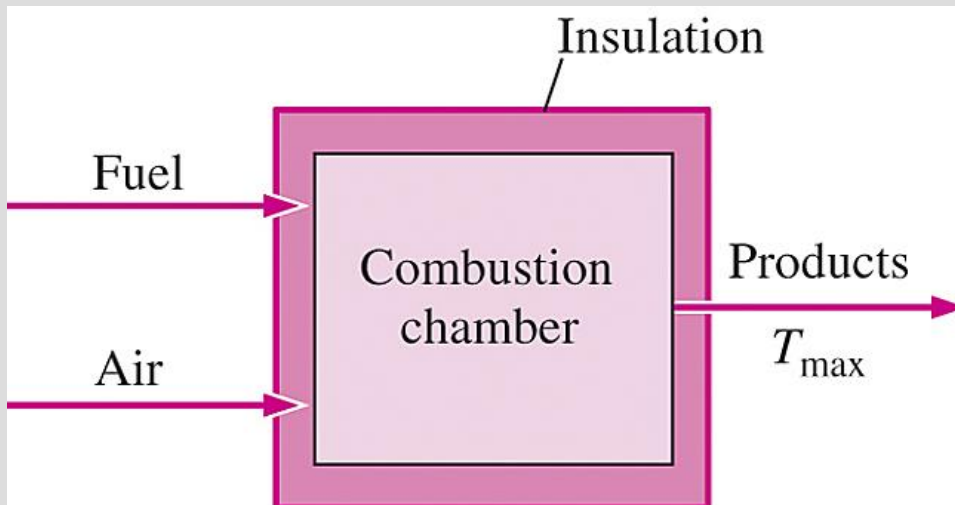
ADIABATIC FLAME TEMPERATURE

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.**

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

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

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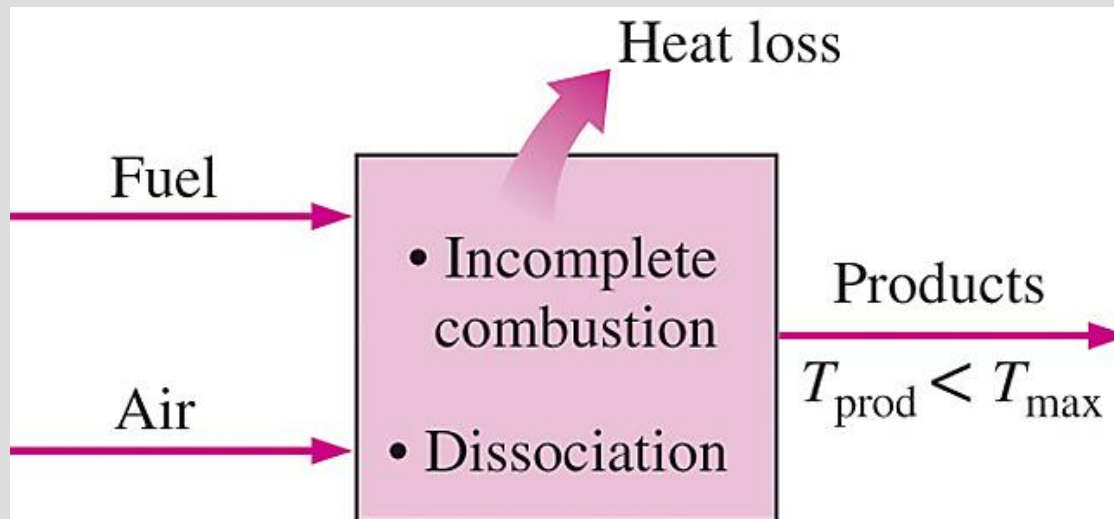

The temperature of a combustion chamber becomes maximum when combustion is complete and no heat is lost to the surroundings ($Q = 0$).

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.*

Heat loss

Fuel

Air

• Incomplete combustion

• Dissociation

Products

$T_{prod} < T_{max}$

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

ENTROPY CHANGE OF REACTING SYSTEMS

$$\underbrace{S_{\text{in}} - S_{\text{out}}}_{\substack{\text{Net entropy transfer} \\ \text{by heat and mass}}} + \underbrace{S_{\text{gen}}}_{\substack{\text{Entropy} \\ \text{generation}}} = \underbrace{\Delta S_{\text{system}}}_{\substack{\text{Change} \\ \text{in entropy}}} \quad (\text{kJ/K})$$
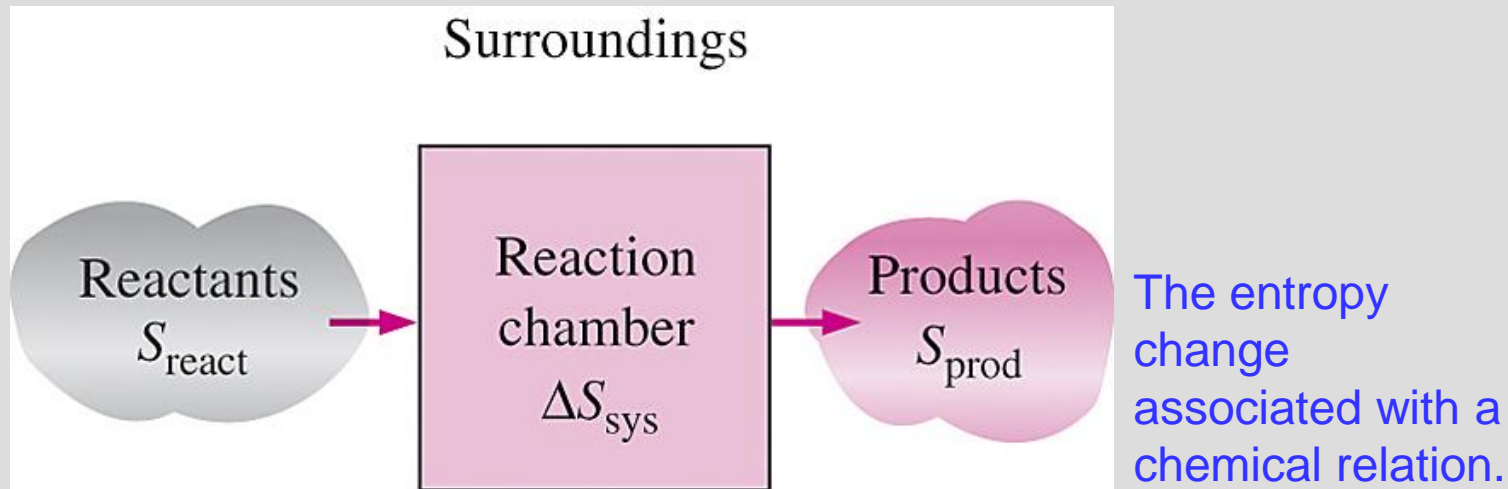
entropy balance for *any system* (including reacting systems) undergoing *any process*

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

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

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

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

The entropy change associated with a chemical relation.

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$$\bar{s}(T,P) = \bar{s}°(T,P_0) - R_u \ln \frac{P}{P_0}$$

Entropy of a component

$P_0 = 1$ atm

P_i partial pressure

$$\bar{s}_i(T,P_i) = \bar{s}°_i(T,P_0) - R_u \ln \frac{y_i P_m}{P_0} \qquad (\text{kJ/kmol} \cdot \text{K})$$

y_i mole fraction

P_m total pressure of mixture.

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

The absolute entropy values are listed in Tables A–18 through A–25 for various ideal gases at the specified temperature and *at a pressure of 1 atm*. The absolute entropy values for various fuels are listed in Table A–26 at the standard reference state of 25°C and 1 atm.

At a specified temperature, the absolute entropy of an ideal gas at pressures other than $P_0 = 1$ atm can be determined by subtracting $R_u \ln (P/P_0)$ from the tabulated value at 1 atm.

T

P

$P_0 = 1$ atm

$\bar{s}(T,P)$

$\bar{s}°(T,P_0)$
(Tabulated)

T

$\bar{s}$

$$\Delta\bar{s} = -R_u \ln \frac{P}{P_0}$$
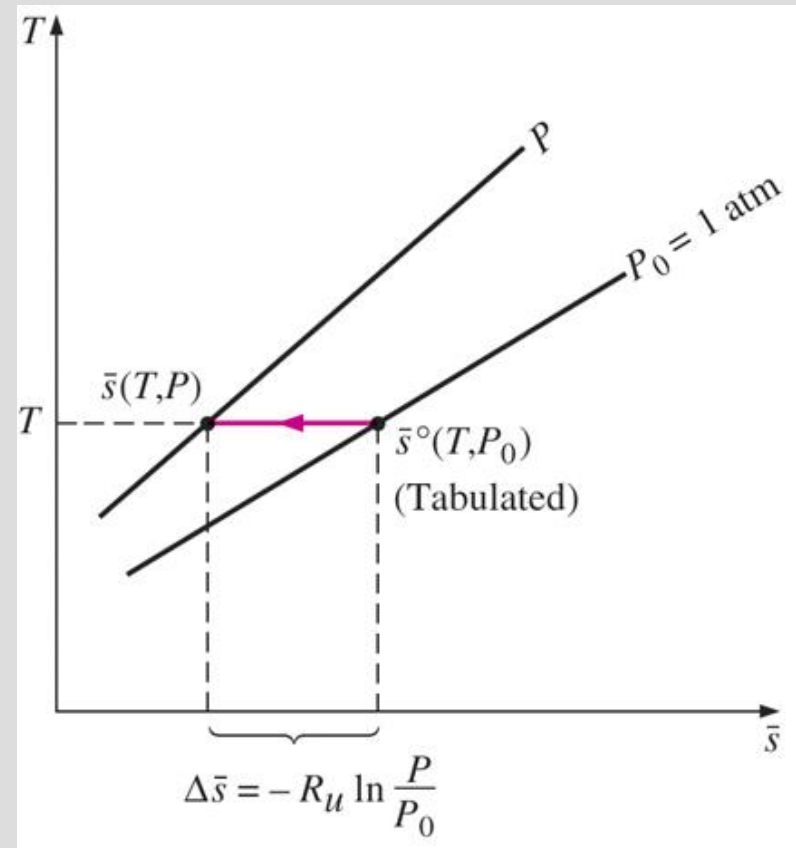
SECOND-LAW ANALYSIS OF REACTING SYSTEMS

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

Exergy destruction

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

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

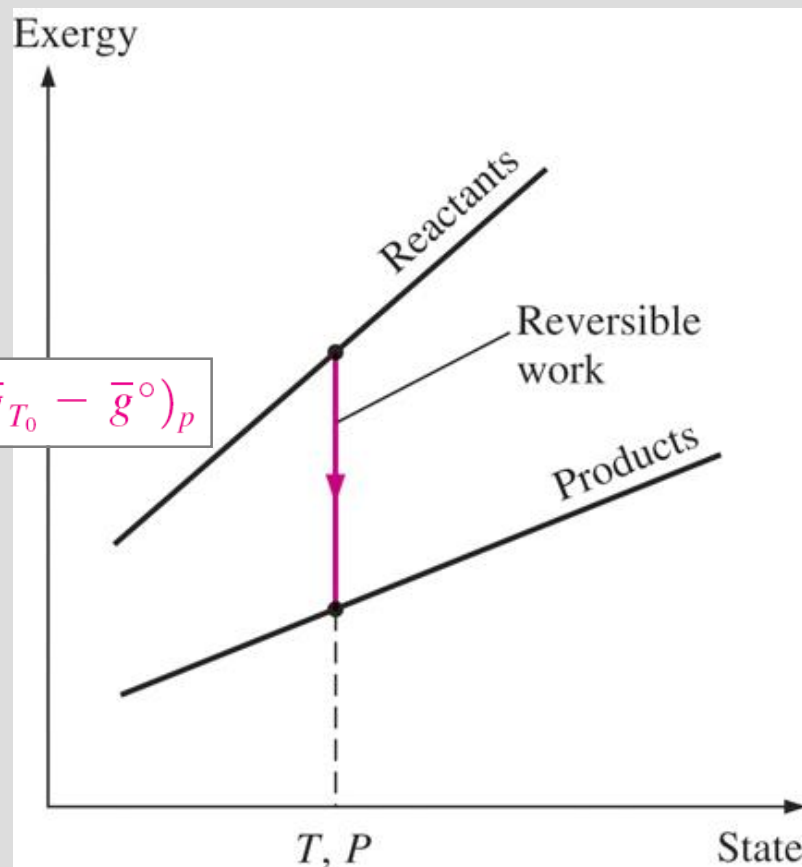When both the reactants and the products are at T_0

$$\bar{h} - T_0\bar{s} = (\bar{h} - T_0\bar{s})_{T_0} = \bar{g}_0$$

Gibbs function

$$W_{\text{rev}} = \sum N_r \bar{g}_{0,r} - \sum N_p \bar{g}_{0,p}$$

$$W_{\text{rev}} = \sum N_r(\bar{g}_f^\circ + \bar{g}_{T_0} - \bar{g}^\circ)_r - \sum N_p(\bar{g}_f^\circ + \bar{g}_{T_0} - \bar{g}^\circ)_p$$
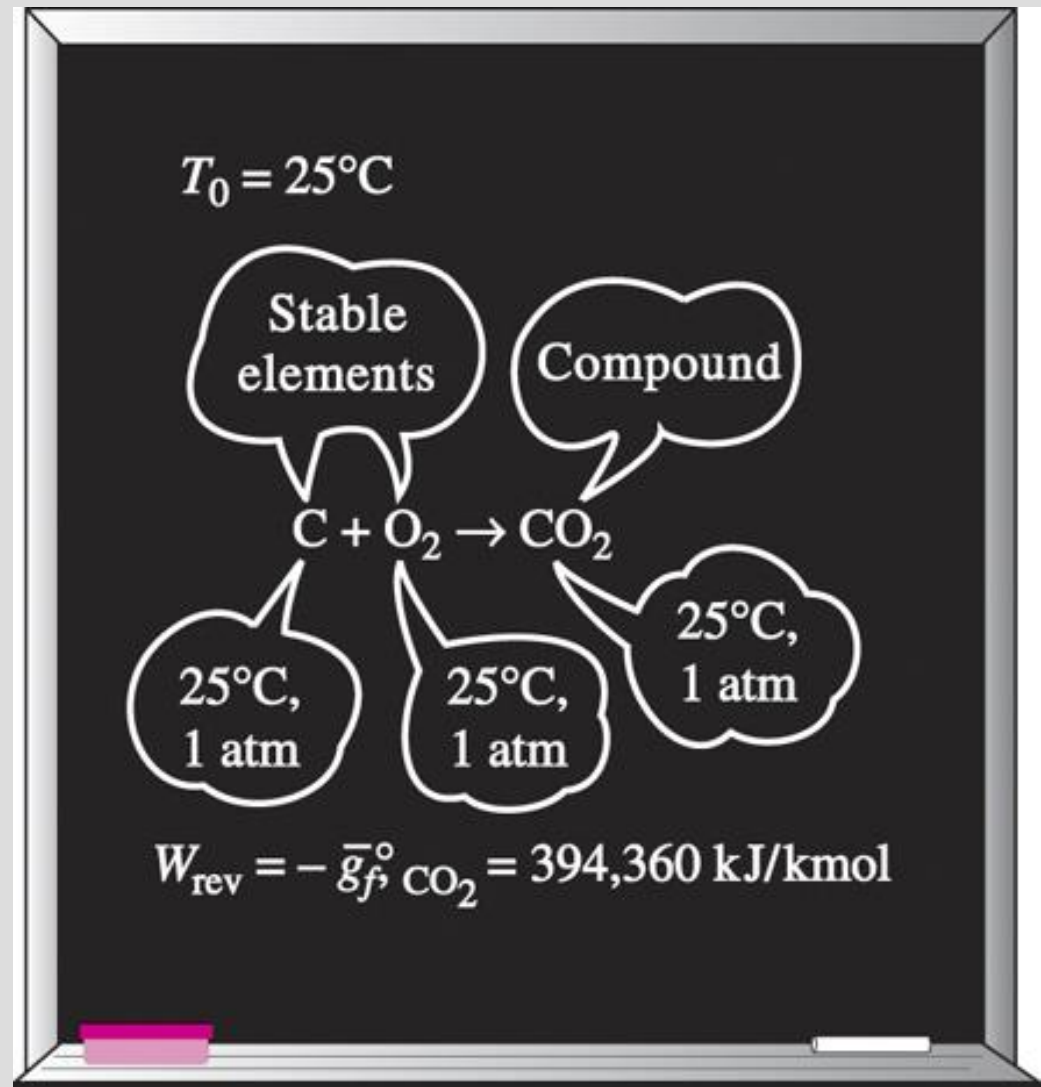
The difference between the exergy of the reactants and of the products during a chemical reaction is the reversible work associated with that reaction.

For the very special case of $T_{react} = T_{prod} = T_0 = 25°C$

$$W_{rev} = \sum N_r \bar{g}^{\circ}_{f,r} - \sum n_p \bar{g}^{\circ}_{f,p} \qquad (kJ)$$

The negative of the Gibbs function of formation of a compound at 25°C, 1 atm represents the reversible work associated with the formation of that compound from its stable elements at 25°C, 1 atm in an environment that is at 25°C, 1 atm.

$T_0 = 25°C$

Stable elements

Compound

$$C + O_2 \rightarrow CO_2$$

25°C, 1 atm

25°C, 1 atm

25°C, 1 atm

$$W_{rev} = -\bar{g}^{\circ}_{f, CO_2} = 394{,}360 \ kJ/kmol$$

Summary

- Fuels and combustion

- Theoretical and actual combustion processes

- Enthalpy of formation and enthalpy of combustion

- First-law analysis of reacting systems
  - ✓ Steady-flow systems
  - ✓ Closed systems

- Adiabatic flame temperature

- Entropy change of reacting systems

- Second-law analysis of reacting systems