

ESO 201A: Thermodynamics

2016-2017-I semester

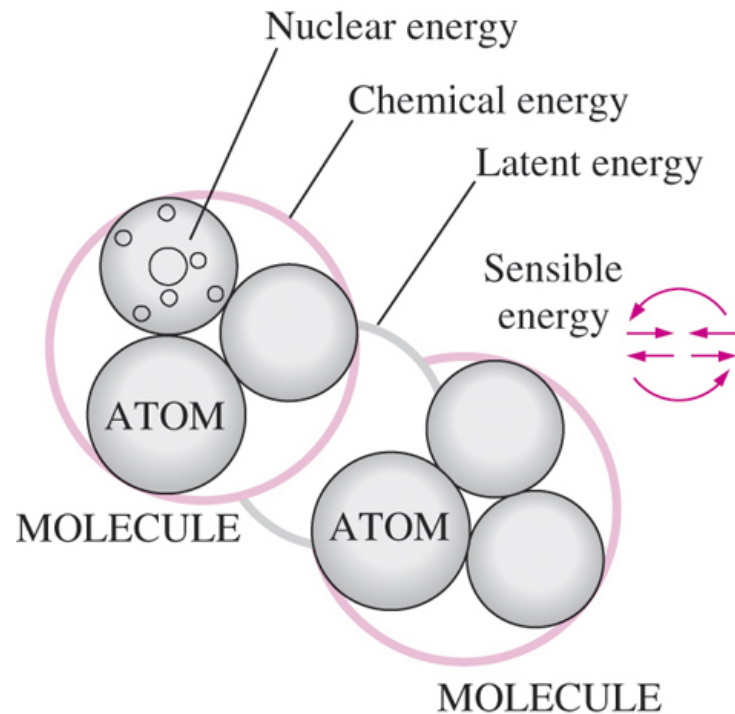
Chemical Reaction: part 3

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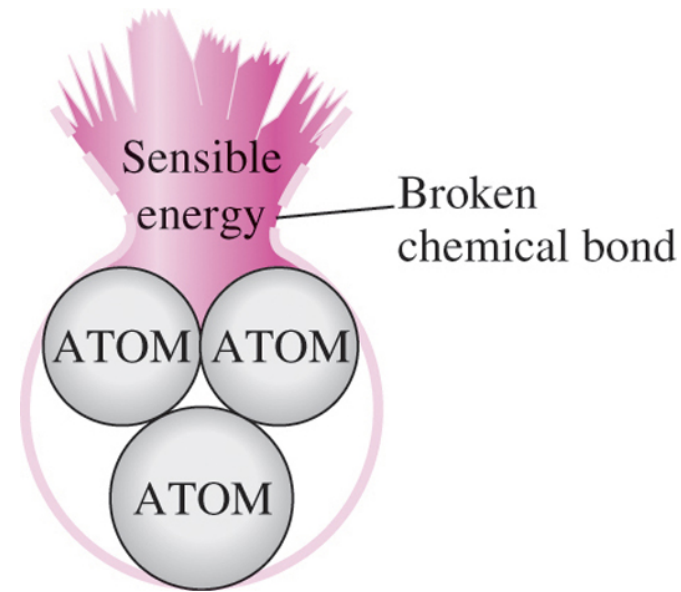
Learning Objectives

- 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
- 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.

Theoretical and Actual Combustion Processes



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.

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:

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

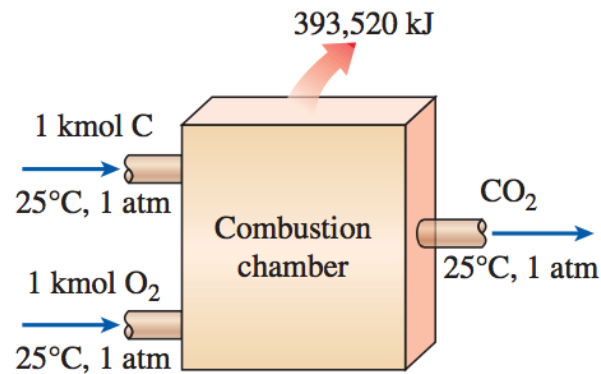
Enthalpy of formation and combustion

- In thermodynamics- changes in energy of a system during a process is of importance.
- Reference state does not effect the results if there is no changes in chemical composition.
- When analyzing reacting systems, we must use property values relative to the standard reference state **as composition of the system is different at the end of the process.** Thus, it is necessary to have a common reference state for all substances.
- The chosen reference state is 25° C 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°).
- We can use the existing tables by subtracting the property values at the standard reference state from the values at the specified state.

$$\bar{h}_{500\text{ K}} - \bar{h}^\circ = 14,581 - 8669 = 5912 \text{ kJ/kmol.}$$

The ideal-gas enthalpy of N_2 at 500 K relative to the standard reference state:

Enthalpy of formation and combustion



Applying the first law to this process, we have

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

An exothermic reaction

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.

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

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

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.

Enthalpy of formation and combustion

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.

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.

$$\bar{h}_{f,\text{CO}_2}^\circ = -393,520 \text{ kJ/kmol}$$

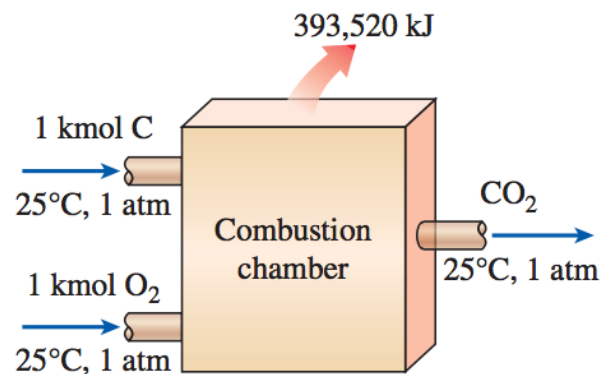


TABLE A-26

Enthalpy of formation, Gibbs function of formation, and absolute entropy at 25°C , 1 atm

Substance	Formula	\bar{h}_f° kJ/kmol	\bar{g}_f° kJ/kmol	\bar{s}° kJ/kmol·K
Carbon	C(s)	0	0	5.74
Hydrogen	$\text{H}_2(\text{g})$	0	0	130.68
Nitrogen	$\text{N}_2(\text{g})$	0	0	191.61
Oxygen	$\text{O}_2(\text{g})$	0	0	205.04
Carbon monoxide	CO(g)	-110,530	-137,150	197.65
Carbon dioxide	$\text{CO}_2(\text{g})$	-393,520	-394,360	213.80
Water vapor	$\text{H}_2\text{O(g)}$	-241,820	-228,590	188.83
Water	$\text{H}_2\text{O(l)}$	-285,830	-237,180	69.92
Hydrogen peroxide	$\text{H}_2\text{O}_2(\text{g})$	-136,310	-105,600	232.63
Ammonia	$\text{NH}_3(\text{g})$	-46,190	-16,590	192.33
Methane	$\text{CH}_4(\text{g})$	-74,850	-50,790	186.16
Acetylene	$\text{C}_2\text{H}_2(\text{g})$	+226,730	+209,170	200.85
Ethylene	$\text{C}_2\text{H}_4(\text{g})$	+52,280	+68,120	219.83
Ethane	$\text{C}_2\text{H}_6(\text{g})$	-84,680	-32,890	229.49
Propylene	$\text{C}_3\text{H}_6(\text{g})$	+20,410	+62,720	266.94
Propane	$\text{C}_3\text{H}_8(\text{g})$	-103,850	-23,490	269.91
n-Butane	$\text{C}_4\text{H}_{10}(\text{g})$	-126,150	-15,710	310.12
n-Octane	$\text{C}_8\text{H}_{18}(\text{g})$	-208,450	+16,530	466.72

Enthalpy of formation and combustion

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.

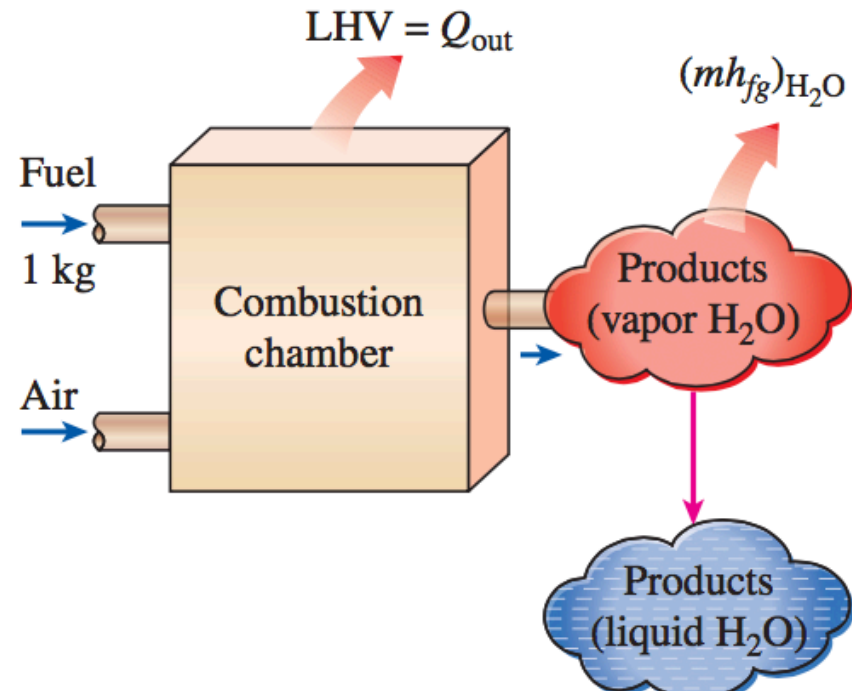
The heating value of a fuel is equal to the absolute value of the enthalpy of combustion of the fuel.

$$\text{Heating value} = |h_c| \quad (\text{kJ/kg fuel})$$

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.

$$\text{HHV} = \text{LHV} + (mh_{fg})_{\text{H}_2\text{O}} \quad (\text{kJ/kg fuel})$$

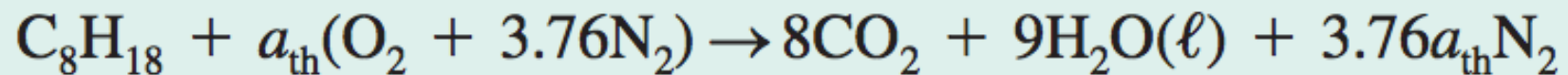


For the fuels with variable composition (i.e., coal, natural gas, fuel oil), the heating value may be determined by burning them directly in a **bomb calorimeter**.

Example

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.

The stoichiometric equation for this reaction is



- Both the reactants and the products are at the standard reference state of 25°C and 1 atm.
- N_2 and O_2 are stable elements, and thus their enthalpy of formation is zero

$$\begin{aligned}\bar{h}_C &= H_{\text{prod}} - H_{\text{react}} \\ &= \sum N_p \bar{h}_{f,p}^\circ - \sum N_r \bar{h}_{f,r}^\circ = (N \bar{h}_f^\circ)_{\text{CO}_2} + (N \bar{h}_f^\circ)_{\text{H}_2\text{O}} - (N \bar{h}_f^\circ)_{\text{C}_8\text{H}_{18}}\end{aligned}$$

Example

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$$\begin{aligned}
 \bar{h}_C &= (8 \text{ kmol})(-393,520 \text{ kJ/kmol}) + (9 \text{ kmol})(-285,830 \text{ kJ/kmol}) \\
 &\quad - (1 \text{ kmol})(-249,950 \text{ kJ/kmol}) \\
 &= \mathbf{-5,471,000 \text{ kJ/kmol C}_8\text{H}_{18}} = \mathbf{-47,891 \text{ kJ/kg C}_8\text{H}_{18}}
 \end{aligned}$$

First law analysis of reacting systems

The enthalpy of a chemical component at a specified state is the sum of the enthalpy of the component at 25°C, 1 atm, and the sensible enthalpy of the component relative to 25°C, 1 atm.

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

Enthalpy at 25°C, 1 atm

Sensible enthalpy relative to 25°C, 1 atm

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

First law analysis of reacting systems

The general **closed-system** energy balance relation can be expressed for a stationary *chemically reacting closed system* as

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

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

Utilizing the definition of enthalpy: $\bar{u}_f^\circ + \bar{u} - \bar{u}^\circ = \bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{v}$

$$\bar{u} = \bar{h} - P\bar{v}$$

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

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.

First law analysis of reacting systems: Steady Flow Systems

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

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

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

Per mole of fuel basis

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

$N_r=1$ for the fuel, and the other N_r and N_p values can be obtained from the balanced combustion equation.

First law analysis of reacting systems

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

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

where

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

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

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

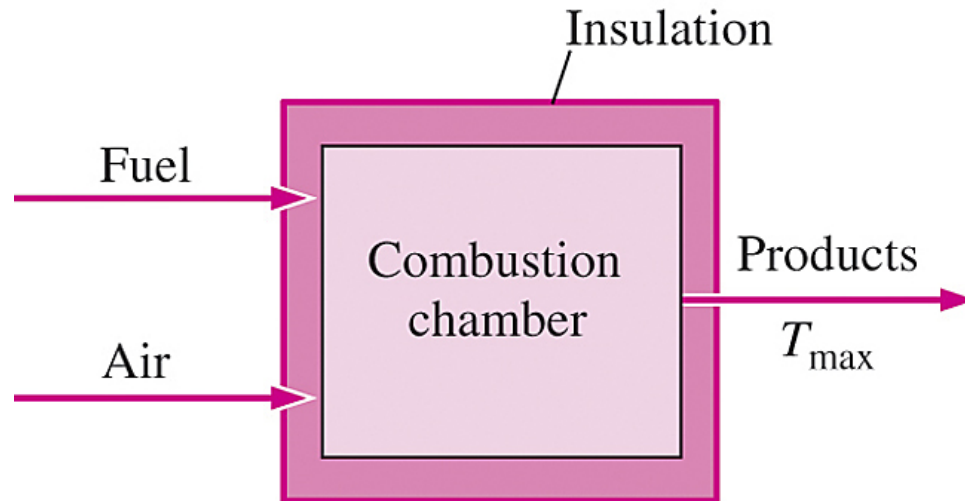
$$Q - W = \bar{h}_C^\circ + \sum N_p(\bar{h} - \bar{h}^\circ)_p - \sum N_r(\bar{h} - \bar{h}^\circ)_r \quad (\text{kJ/kmol})$$

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

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

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**.



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

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

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

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

Adiabatic flame temperature

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.

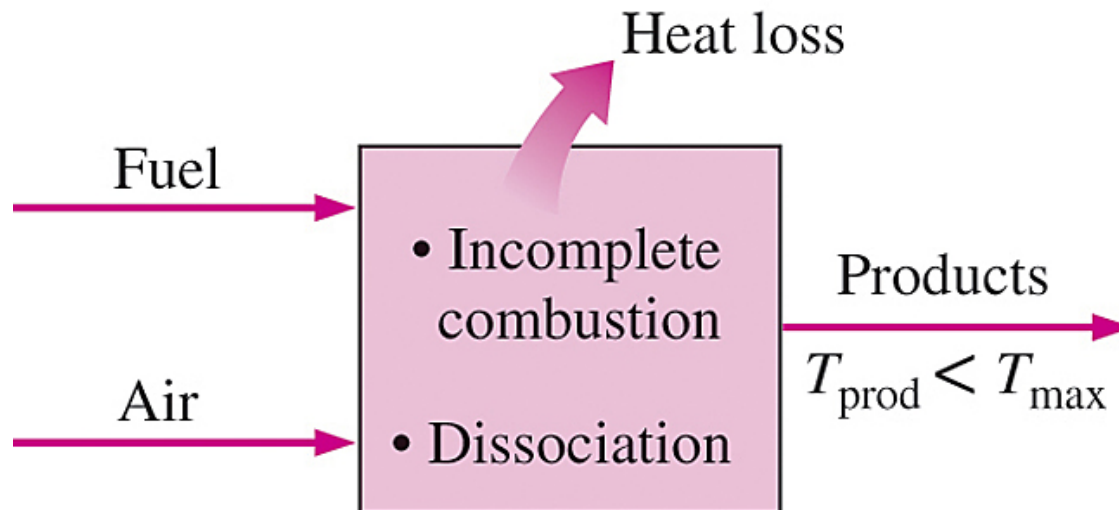
The adiabatic flame temperature is an important consideration in the design of combustion chambers, gas turbines, and nozzles.

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

Adiabatic flame temperature

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

- combustion is usually incomplete,
- some heat loss takes place,
- some combustion gases dissociate at high temperatures.



The maximum temperature in a combustion chamber can be controlled by adjusting the amount of excess air, which serves as a coolant.

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