Chapter 13

Reacting Mixtures
and Combustion

Learning Outcomes

- ►Demonstrate understanding of key concepts, including complete combustion, theoretical air, enthalpy of formation, and adiabatic flame temperature.
- ►Determine balanced reaction equations for combustion of hydrocarbon fuels.
- ►Apply mass, energy, and entropy balances to closed systems and control volumes involving chemical reactions.
- ►Perform exergy analyses, including chemical exergy and the evaluation of exergetic efficiencies.

Introducing Combustion

- In *combustion reactions*, rapid oxidation of combustible elements of the fuel results in energy release as combustion products are formed.
- Three major combustible elements in common fuels are
  - carbon
  - hydrogen
  - sulfur

Introducing Combustion

- Combustion is *complete* when
  - All carbon present in the fuel is burned to carbon dioxide
  - All hydrogen present is burned to water
  - All sulfur present is burned to sulfur dioxide
  - All other combustible elements are *fully oxidized*
- When these conditions are not fulfilled, combustion is *incomplete*.

Introducing Combustion

Example: Determine the balanced reaction equation for complete combustion of methane (CH_4) with oxygen (O_2).

►For complete combustion, the products contain only carbon dioxide and water:

$$CH_4 + aO_2 \rightarrow bCO_2 + cH_2O$$

where a, b, c denote the moles of O_2, CO_2, and H_2O, respectively, each per mole of CH_4.

►Applying conservation of mass to carbon, hydrogen, and oxygen: $C: 1 = b$ $H: 4 = 2c$ $O: 2a = 2b + c$

►Solving these equations, the ***balanced*** reaction equation is

$$\boxed{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O}$$

Modeling Combustion Air

- ► Oxygen is required in every combustion reaction. In most combustion applications, air provides the needed oxygen.
- ► The following model of ***dry air*** is used for simplicity:
  1. All components of dry air other than oxygen are lumped together with nitrogen. With this idealization, air is considered to be **21%** $\mathbf{O_2}$ and **79%** $\mathbf{N_2}$ on a molar basis.

     Accordingly, when air supplies the oxygen in a combustion reaction, every mole of $\mathbf{O_2}$ is accompanied by $\mathbf{0.79/0.21 = 3.76}$ moles of $\mathbf{N_2}$.
  2. The nitrogen present in the air is assumed inert.
  3. The molecular weight of dry air is 28.97.
- ► When ***moist air*** is used in combustion, the water vapor present in the air should be considered in writing the combustion equation.

Air-Fuel Ratio

- ▶ The air-fuel ratio is the ratio of the amount of air in a combustion reaction to the amount of fuel.
- ▶ The air-fuel ratio can be written on a molar basis:

$$\overline{AF} = \frac{\text{moles of air}}{\text{moles of fuel}}$$

or on a mass basis:

$$AF = \frac{\text{mass of air}}{\text{mass of fuel}}$$

- ▶ Conversion between these values is accomplished using the molecular weights of air, M_{air}, and fuel, M_{fuel},

$$AF = \overline{AF}\left(\frac{M_{\text{air}}}{M_{\text{fuel}}}\right) \qquad \textbf{(Eq. 13.2)}$$

- ▶ The fuel-air ratio is the reciprocal of the air-fuel ratio.

Theoretical Amount of Air

- ►The theoretical amount of air is the minimum amount of air that supplies sufficient oxygen for the complete combustion of all the carbon, hydrogen, and sulfur present in the fuel.
- ►For complete combustion with the theoretical amount of air, the products consist of $\mathbf{CO_2}$, $\mathbf{H_2O}$, and $\mathbf{SO_2}$ plus nitrogen present in the reactants. No free oxygen, $\mathbf{O_2}$, appears in the products.
- ►Normally the amount of air supplied is either greater than or less than the theoretical amount. The amount of air actually supplied is commonly expressed as
  - ►A **percent of theoretical air** – e.g., **150%** of theoretical air equals **1.5** times the theoretical amount.
  - ►A **percent excess** (**or percent deficiency**) **of air** – e.g., **50%** excess air equals **150%** of theoretical air.

Exploring Combustion Concepts

►The balanced chemical equation for complete combustion of methane with the theoretical amount of air is

$$CH_4 + \boxed{2}(O_2 + \boxed{3.76}N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2 \quad \text{(Eq. 13.4)}$$

- ►The coefficient **2** before the term $(O_2 + 3.76\, N_2)$ is the number of moles of O_2 in the combustion air per mole of fuel.
- ►The number of moles of N_2 in the combustion air per mole of fuel is 2×3.76.
- ►The amount of combustion air per mole of fuel is the sum,

$$2 + 2 \times 3.76 = 2(4.76) = 9.52$$

- ►This is the air-fuel ratio on a molar basis: $\overline{AF} = 9.52/1$.

Exploring Combustion Concepts

►The balanced chemical equation for complete combustion of methane with **150%** theoretical air is

$$\mathrm{CH_4} + \boxed{(1.5)}(2)\,(\mathrm{O_2} + 3.76\,\mathrm{N_2}) \rightarrow \mathrm{CO_2} + 2\mathrm{H_2O} + \boxed{\mathrm{O_2}} + \boxed{11.28\,\mathrm{N_2}}$$

►The amount of air per mole of fuel is **1.5** times the theoretical amount determined by **Eq. 13.4**.

►The excess air supplied appears in the products as $\mathrm{O_2}$ and as a greater amount of $\mathrm{N_2}$ than in **Eq. 13.4**, based on the theoretical amount of air.

►The air-fuel ratio on a molar basis is,

$$\overline{AF} = (1.5)(2)(4.76)/1 = 14.28/1$$

Dry Product Analysis

►In practical applications, combustion is generally ***incomplete***.

►The products of combustion of actual combustion processes and their relative amounts can be determined only by measurement.

►Certain devices for measuring the composition of combustion products report the analysis on a ***dry product analysis*** basis where the mole fractions are given for all products except water.

Dry Product Analysis

Example: Ethanol (**C_2H_5OH**) is burned with air to give products with the dry molar analysis **3.16% CO_2**, **16.6% CO**, **80.24% N_2**. Determine the balanced chemical reaction.

►Basing the solution for convenience on 100 moles of dry products, the reaction equation reads:

$$\boxed{a}\,C_2H_5OH + b(O_2 + 3.76N_2) \rightarrow 3.16CO_2 + 16.6CO + 80.24N_2 + \boxed{cH_2O}$$

where ***a*** denotes the moles of fuel required for **100** moles of dry products.

Also note that a term accounting for the water formed in this reaction must be included.

Dry Product Analysis

$$aC_2H_5OH + b(O_2 + 3.76N_2) \rightarrow 3.16CO_2 + 16.6CO + 80.24N_2 + cH_2O$$

► Applying conservation of mass

$C: \quad 2a = 3.16 + 16.6 \rightarrow a = 9.88$

$H: \quad 6a = 2c \rightarrow c = 29.64$

$N: \quad 3.76b = 80.24 \rightarrow b = 21.34$

Checking:

$O: \quad a + 2b = 3.16(2) + 16.6 + c$

$52.56 = 52.56$ ✓

► The ***balanced*** reaction equation is

$$9.88C_2H_5OH+21.34(O_2+3.76N_2)\rightarrow 3.16CO_2+16.6CO+80.24N_2+29.64H_2O$$

► Expressing this on a per mole of fuel basis

$$\boxed{C_2H_5OH + 2.16(O_2 + 3.76N_2) \rightarrow 0.32CO_2 + 1.68CO + 8.12N_2 + 3H_2O}$$

Energy and Entropy Balances for Reacting Systems

- ►The forms of the energy and entropy balances used thus far remain valid for reacting systems. Still, there are some special aspects worth noting.
- ►Combustion air and (frequently) products of combustion are each modeled as ideal gas mixtures. Accordingly, the ideal gas mixture principles summarized in Table 13.1 play a role.

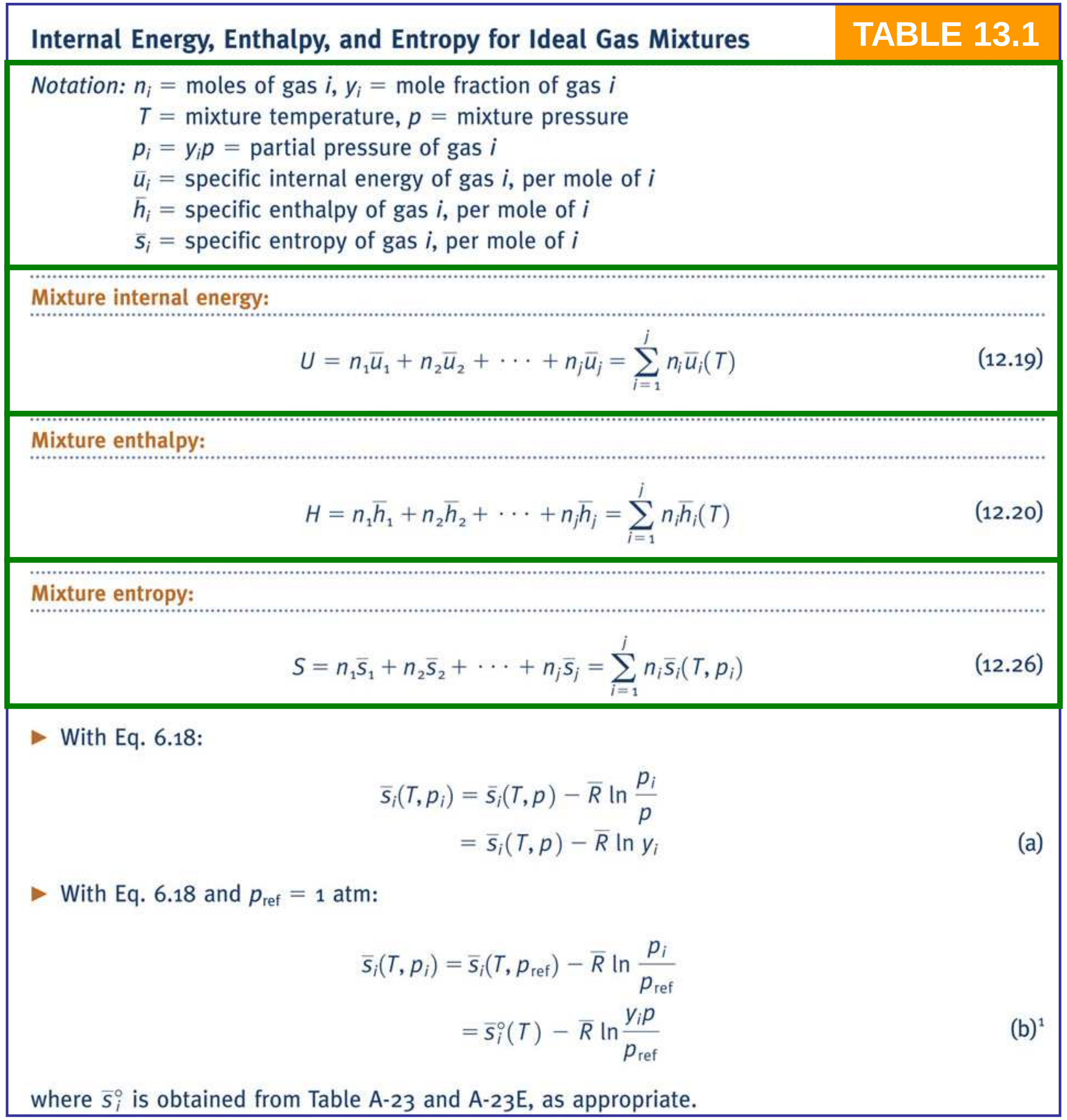


TABLE 13.1

Internal Energy, Enthalpy, and Entropy for Ideal Gas Mixtures

Notation: n_i = moles of gas i, y_i = mole fraction of gas i
T = mixture temperature, p = mixture pressure
$p_i = y_i p$ = partial pressure of gas i
$\bar{u}_i$ = specific internal energy of gas i, per mole of i
$\bar{h}_i$ = specific enthalpy of gas i, per mole of i
$\bar{s}_i$ = specific entropy of gas i, per mole of i

Mixture internal energy:

$$U = n_1\bar{u}_1 + n_2\bar{u}_2 + \cdots + n_j\bar{u}_j = \sum_{i=1}^{j} n_i\bar{u}_i(T) \qquad (12.19)$$

Mixture enthalpy:

$$H = n_1\bar{h}_1 + n_2\bar{h}_2 + \cdots + n_j\bar{h}_j = \sum_{i=1}^{j} n_i\bar{h}_i(T) \qquad (12.20)$$

Mixture entropy:

$$S = n_1\bar{s}_1 + n_2\bar{s}_2 + \cdots + n_j\bar{s}_j = \sum_{i=1}^{j} n_i\bar{s}_i(T, p_i) \qquad (12.26)$$

► With Eq. 6.18:

$$\begin{aligned}\bar{s}_i(T, p_i) &= \bar{s}_i(T, p) - \bar{R}\ln\frac{p_i}{p} \\ &= \bar{s}_i(T, p) - \bar{R}\ln y_i \qquad \text{(a)}\end{aligned}$$

► With Eq. 6.18 and $p_{\text{ref}} = 1$ atm:

$$\begin{aligned}\bar{s}_i(T, p_i) &= \bar{s}_i(T, p_{\text{ref}}) - \bar{R}\ln\frac{p_i}{p_{\text{ref}}} \\ &= \bar{s}_i^\circ(T) - \bar{R}\ln\frac{y_i p}{p_{\text{ref}}} \qquad \text{(b)}^1\end{aligned}$$

where $\bar{s}_i^\circ$ is obtained from Table A-23 and A-23E, as appropriate.

Energy and Entropy Balances for Reacting Systems

► For reacting systems, the methods used for evaluating specific enthalpy and specific entropy differ fundamentally from the practices used thus far in nonreacting applications. This brings in two new concepts:

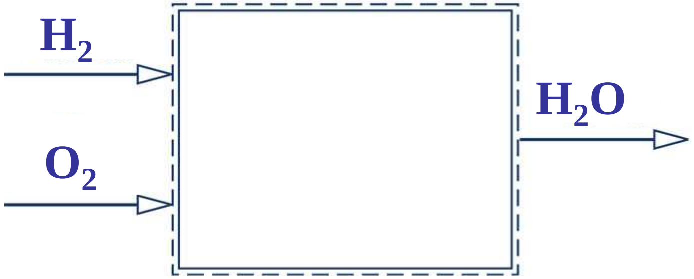
- ► Enthalpy of formation
- ► Absolute entropy

► A simple example illustrates the need for revising the way enthalpy and entropy are evaluated in reacting systems. The figure shows a control volume in which hydrogen and oxygen enter, each as ideal gases, and react to form liquid water according to

$$\boxed{H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O}$$

Energy and Entropy Balances for Reacting Systems

$$\boxed{H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O}$$

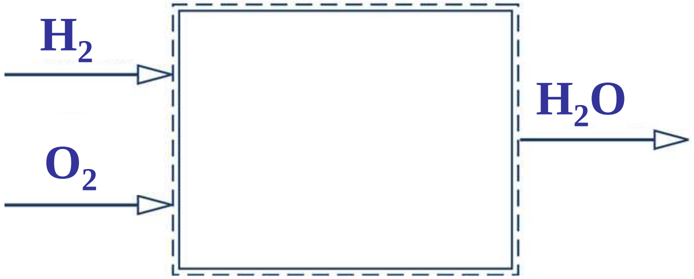


► To apply an energy balance to the control volume, we might think of using enthalpy data from the ***steam tables*** for liquid water and from Table A-23 for the gases.

► However, since those tables use ***arbitrary datums*** to assign enthalpy values, they must be used ***only*** to determine ***differences*** in enthalpy between two states, for then and only then do the arbitrary datums cancel – see Sec. 3.6.3.

Energy and Entropy Balances for Reacting Systems

$$\boxed{H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O}$$



- For the case under consideration, H_2 and O_2 enter the control volume but do not exit, and liquid water exits but does not enter. Accordingly, enthalpy differences from inlet to exit do not arise for each of these substances when applying an energy balance to the control volume. For each it is necessary to assign enthalpy values in a way that the ***common*** datum cancels. This is achieved using the ***enthalpy of formation***.
- Like considerations apply when evaluating entropy values for substances in reacting systems; for them ***absolute entropy*** values are required.

Evaluating Enthalpy for Reactive Systems

►An enthalpy datum for the study of reacting systems is established by assigning a value of zero to the enthalpy of **C**, $\mathbf{H_2}$, $\mathbf{N_2}$, $\mathbf{O_2}$, and other stable elements at the ***standard reference state*** defined by $T_{\mathrm{ref}} = 298.15\ \mathrm{K}\ (25^{\circ}\mathrm{C})$ and $p_{\mathrm{ref}} = 1\mathrm{atm}$.

►The enthalpy of a ***compound*** at the standard state equals its ***enthalpy of formation***, denoted $\bar{h}_f^{\circ}$.

►The enthalpy of formation is the energy released or absorbed when the compound is formed from its elements, the compound and elements all being at T_{ref} and p_{ref}.

Evaluating Enthalpy for Reactive Systems

►Table A-25 gives values of the enthalpy of formation in kJ/kmol.

►As indicated by the table heading these data apply only to the standard state, **298 K**, **1 atm**.

►A zero value is assigned to the enthalpy of formation for each of the first four substances.

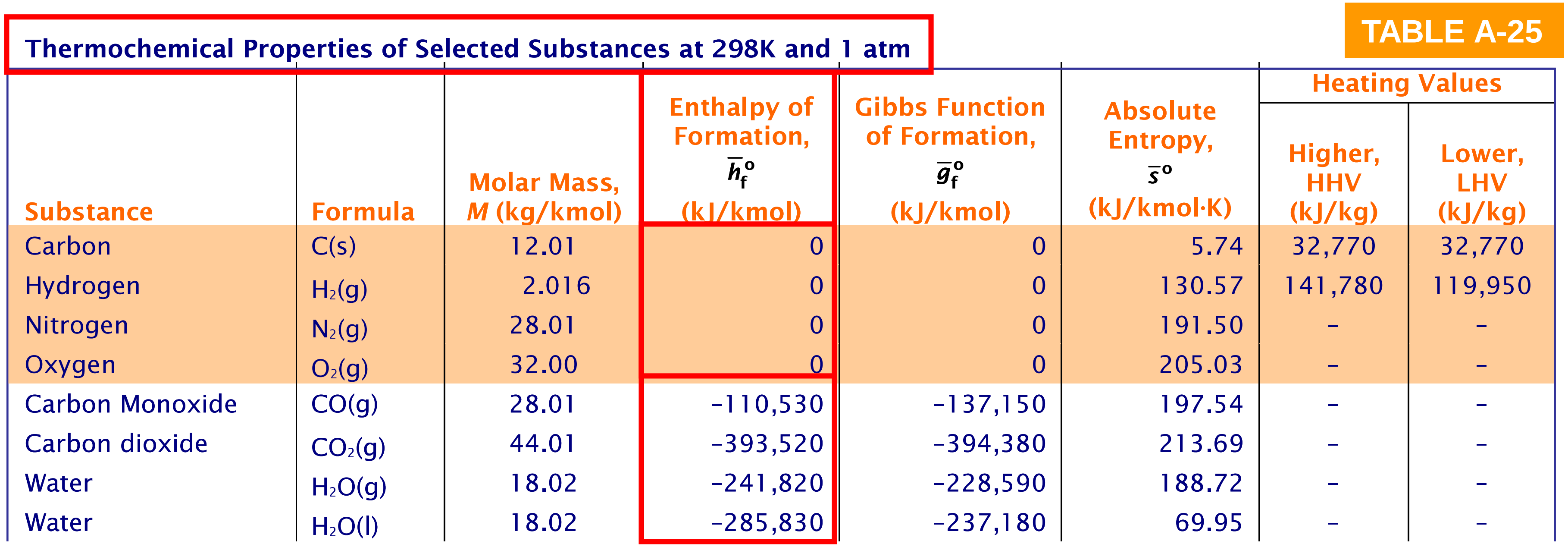


TABLE A-25

Thermochemical Properties of Selected Substances at 298K and 1 atm

Substance	Formula	Molar Mass, M (kg/kmol)	Enthalpy of Formation, $\bar{h}_f^o$ (kJ/kmol)	Gibbs Function of Formation, $\bar{g}_f^o$ (kJ/kmol)	Absolute Entropy, $\bar{s}^o$ (kJ/kmol·K)	Heating Values	
						Higher, HHV (kJ/kg)	Lower, LHV (kJ/kg)
Carbon	$C(s)$	12.01	0	0	5.74	32,770	32,770
Hydrogen	$H_2(g)$	2.016	0	0	130.57	141,780	119,950
Nitrogen	$N_2(g)$	28.01	0	0	191.50	–	–
Oxygen	$O_2(g)$	32.00	0	0	205.03	–	–
Carbon Monoxide	$CO(g)$	28.01	−110,530	−137,150	197.54	–	–
Carbon dioxide	$CO_2(g)$	44.01	−393,520	−394,380	213.69	–	–
Water	$H_2O(g)$	18.02	−241,820	−228,590	188.72	–	–
Water	$H_2O(l)$	18.02	−285,830	−237,180	69.95	–	–

Evaluating Enthalpy for Reactive Systems

►Nonzero values apply to all other substances, where a minus sign correspond to an ***exothermic*** reaction when the compound is formed from its elements. A positive value of the enthalpy of formation corresponds to an ***endothermic*** reaction when the compound is formed from its elements.

TABLE A-25

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Carbon Monoxide	$CO(g)$	28.01	–110,530	–137,150	197.54	–	–
Carbon dioxide	$CO_2(g)$	44.01	–393,520	–394,380	213.69	–	–
Water	$H_2O(g)$	18.02	–241,820	–228,590	188.72	–	–
Water	$H_2O(l)$	18.02	–285,830	–237,180	69.95	–	–
Hydrogen peroxide	$H_2O_2(g)$	34.02	–136,310	–105,600	232.63	–	–
Ammonia	$NH_3(g)$	17.03	–46,190	–16,590	192.33	–	–
Oxygen	$O(g)$	16.00	249,170	231,770	160.95	–	–
Hydrogen	$H(g)$	1.008	218,000	203,290	114.61	–	–

Evaluating Enthalpy for Reactive Systems

- The specific enthalpy of a compound at a state where temperature is T and pressure is p is determined from

$$\bar{h}(T,p) = \bar{h}_f^\circ + [\bar{h}(T,p) - \bar{h}(T_{ref}, p_{ref})] = \boxed{\bar{h}_f^\circ} + \boxed{\Delta\bar{h}} \qquad \textbf{(Eq. 13.9)}$$

That is, the enthalpy of a compound is composed of

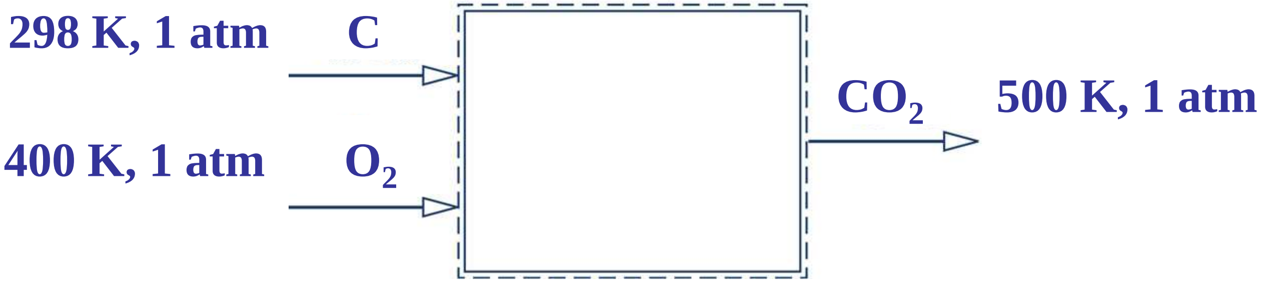
  - $\bar{h}_f^o$ associated with the formation of the compound from its elements. This is obtained from Table A-25.
  - $\Delta\bar{h}$ associated with the change in state from the standard state to the state where temperature is T and the pressure is p. Since this term is a difference at fixed composition, it can be evaluated from the ideal gas tables, steam tables, or other tables, as appropriate.

Using the Enthalpy of Formation Concept with the Control Volume Energy Rate Balance

- ►The enthalpy of formation concept enables the control volume energy rate balance to be implemented for engineering applications involving combustion, including
  - ►Calculation of heating values (Sec. 13.2.3)
  - ►Calculation of adiabatic flame temperature (Sec. 13.3)
- ►The following example provides a specific illustration showing use of the enthalpy of formation.

Example

►Pulverized coal (assume carbon) enters a combustor at **298 K**, **1 atm** and burns completely with O_2 entering at **400 K**, **1 atm**. A stream of carbon dioxide exits at **500 K**, **1 atm**. For a control volume at steady state enclosing the reactor, evaluate the rate of heat transfer, in kJ per kmol of coal entering. Assume the ideal gas model for O_2 and CO_2, and neglect kinetic and potential energy effects.



$$\boxed{C + O_2 \rightarrow CO_2}$$

Example

$$\boxed{C + O_2 \rightarrow CO_2}$$

- ► The energy rate balance on a molar basis is:

$$0 = \dot{Q}_{cv} - \cancel{\dot{W}_{cv}} + \dot{n}_C \bar{h}_C + \dot{n}_{O_2} \bar{h}_{O_2} - \dot{n}_{CO_2} \bar{h}_{CO_2}$$

- ► $\dot{W}_{cv} = 0$, and kinetic and potential energy effects are neglected.

- ► Solving for the heat transfer per mole of coal, and noting from the reaction equation that the molar flow rates are equal

$$\frac{\dot{Q}_{cv}}{\dot{n}_C} = \cancelto{1}{\frac{\dot{n}_{CO_2}}{\dot{n}_C}} \bar{h}_{CO_2} - \bar{h}_C - \cancelto{1}{\frac{\dot{n}_{O_2}}{\dot{n}_C}} \bar{h}_{O_2}$$

Example

$$\frac{\dot{Q}_{cv}}{\dot{n}_C} = \bar{h}_{CO_2} - \boxed{\bar{h}_C} - \bar{h}_{O_2} \qquad \textbf{(1)}$$

- ►Carbon enters at the standard state. With $\bar{h}_f^o$ from Table A-25, **Eq. 13.9** gives

$$\bar{h}_C(298\,\text{K}, 1\,\text{atm}) = \boxed{(\bar{h}_f^o)_C} + \cancel{(\Delta\bar{h})_C}$$

$$\boxed{\bar{h}_C(298\,\text{K}, 1\,\text{atm}) = 0\ \text{kJ/kmol}}$$

TABLE A-25

Thermochemical Properties of Selected Substances at 298K and 1 atm

Substance	Formula	Molar Mass, *M* (kg/kmol)	Enthalpy of Formation, $\bar{h}_f^o$ (kJ/kmol)	Gibbs Function of Formation, $\bar{g}_f^o$ (kJ/kmol)	Absolute Entropy, $\bar{s}^o$ (kJ/kmol·K)	Heating Values: Higher, HHV (kJ/kg)	Heating Values: Lower, LHV (kJ/kg)
Carbon	C(s)	12.01	0	0	5.74	32,770	32,770
Hydrogen	H_2(g)	2.016	0	0	130.57	141,780	119,950
Nitrogen	N_2(g)	28.01	0	0	191.50	–	–

Example

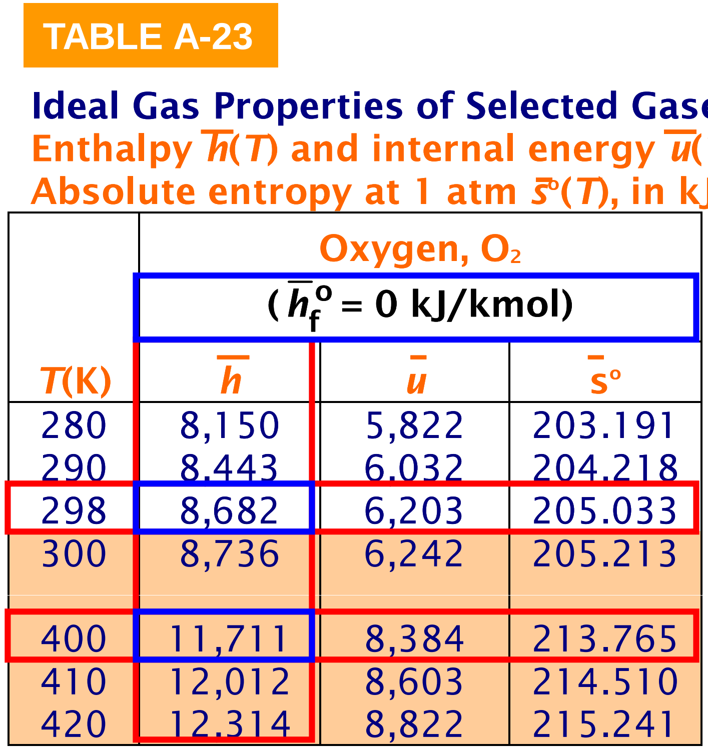


TABLE A-23

Ideal Gas Properties of Selected Gases

Enthalpy $\bar{h}(T)$ and internal energy $\bar{u}(T)$, in kJ/kmol.
Absolute entropy at 1 atm $\bar{s}^\circ(T)$, in kJ/kmol·K.

	Oxygen, O_2		
	($\bar{h}_f^o$ = 0 kJ/kmol)		
T(K)	$\bar{h}$	$\bar{u}$	$\bar{s}^\circ$
280	8,150	5,822	203.191
290	8,443	6,032	204.218
298	8,682	6,203	205.033
300	8,736	6,242	205.213
400	11,711	8,384	213.765
410	12,012	8,603	214.510
420	12,314	8,822	215.241

$$\frac{\dot{Q}_{cv}}{\dot{n}_C} = \bar{h}_{CO_2} - \bar{h}_C - \boxed{\bar{h}_{O_2}} \qquad (1)$$

►Oxygen enters at **400 K**, **1 atm**. With data from Table A-23, **Eq. 13.9** gives

$$\bar{h}_{O_2}(400\,\text{K}, 1\,\text{atm}) = \boxed{(\bar{h}_f^o)_{O_2}} + \boxed{(\Delta\bar{h})_{O_2}}$$

$$\bar{h}_{O_2}(400\,\text{K}, 1\,\text{atm}) = 0 + (11{,}711 - 8{,}682)$$

$$\boxed{\bar{h}_{O_2}(400\,\text{K}, 1\,\text{atm}) = 3{,}029\ \text{kJ/kmol}}$$

Example

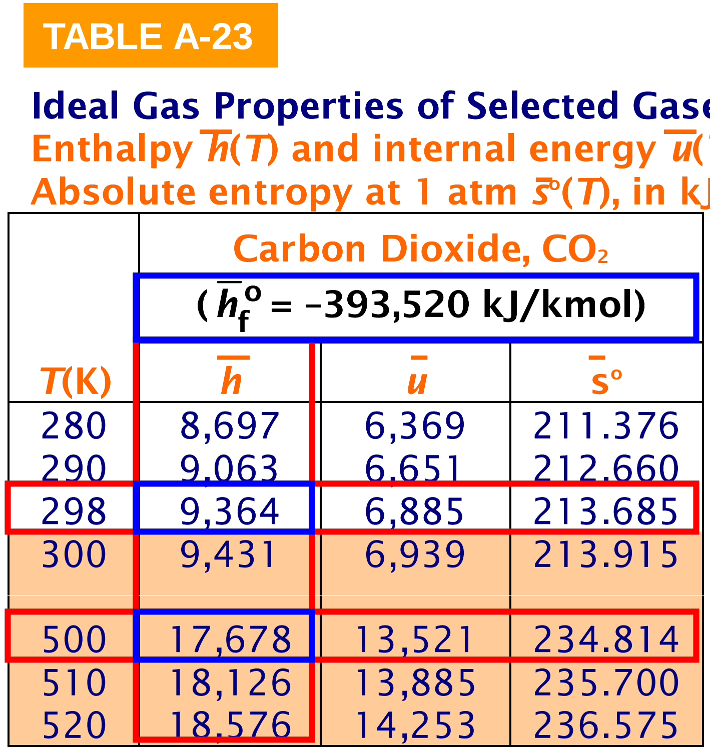


TABLE A-23

Ideal Gas Properties of Selected Gases

Enthalpy $\bar{h}(T)$ and internal energy $\bar{u}(T)$, in kJ/kmol.
Absolute entropy at 1 atm $\bar{s}^{\circ}(T)$, in kJ/kmol·K.

	Carbon Dioxide, CO_2		
	$(\bar{h}_f^{o} = -393{,}520$ kJ/kmol)		
T(K)	$\bar{h}$	$\bar{u}$	$\bar{s}^{\circ}$
280	8,697	6,369	211.376
290	9,063	6,651	212.660
298	9,364	6,885	213.685
300	9,431	6,939	213.915
500	17,678	13,521	234.814
510	18,126	13,885	235.700
520	18,576	14,253	236.575

$$\frac{\dot{Q}_{cv}}{\dot{n}_C} = \boxed{\bar{h}_{CO_2}} - \bar{h}_C - \bar{h}_{O_2} \qquad (1)$$

- ►Carbon dioxide exits at **500 K**, **1 atm**. With data from Table A-23, **Eq. 13.9** gives

$$\bar{h}_{CO_2}(500\,\text{K}, 1\,\text{atm}) = \boxed{(\bar{h}_f^{o})_{CO_2}} + \boxed{(\Delta\bar{h})_{CO_2}}$$

$$\bar{h}_{CO_2}(500\,\text{K}, 1\,\text{atm}) = -393{,}520 + (17{,}678 - 9{,}364)$$

$$\boxed{\bar{h}_{CO_2}(500\,\text{K}, 1\,\text{atm}) = -385{,}206\ \text{kJ/kmol}}$$

Example

$$\boxed{C + O_2 \rightarrow CO_2}$$

298 K, 1 atm C

400 K, 1 atm O_2

CO_2 500 K, 1 atm

► With these values, **Eq. (1)** gives

$$\frac{\dot{Q}_{cv}}{\dot{n}_C} = -385{,}206 - 0 - 3{,}029$$

$$\boxed{\frac{\dot{Q}_{cv}}{\dot{n}_C} = -388{,}235\ \text{kJ/kmol}}$$

► The minus sign indicates heat transfer from the control volume.

Heating Values of Hydrocarbon Fuels

►The ***heating values*** of hydrocarbon fuels have important applications.

►The ***heating value*** of a fuel is the difference between the enthalpy of the reactants and the enthalpy of the products when the fuel burns completely with air, reactants and products being at the same temperature T and pressure p.

Heating Values of Hydrocarbon Fuels

- ►That is, the heating value per mole of fuel

$$= \sum_{\mathrm{R}} n_i \bar{h}_i - \sum_{\mathrm{P}} n_e \bar{h}_e$$

$$= \sum_{\mathrm{R}} n_i \left(\bar{h}_{\mathrm{f}}^{\mathrm{o}} + \Delta\bar{h}\right)_i - \sum_{\mathrm{P}} n_e \left(\bar{h}_{\mathrm{f}}^{\mathrm{o}} + \Delta\bar{h}\right)_e \qquad \mathbf{(1)}$$

where

- ►**R** denotes the reactants and **P** denotes the products.
- ►The ***n*'s** correspond to the coefficients of the reaction equation, each per mole of fuel.

Heating Values of Hydrocarbon Fuels

►Two heating values are recognized by name:

- ►The **higher heating value** (HHV) is obtained when all the water formed by combustion is a liquid.
- ►The **lower heating value** (LHV) is obtained when all the water formed by combustion is a vapor.
- ►The higher heating value exceeds the lower heating value by the energy that would be released were all water in the products condensed to liquid.

Heating Values of Hydrocarbon Fuels

►Heating value data at 298 K, 1 atm are provided in Table A-25 with units of kJ/kg.

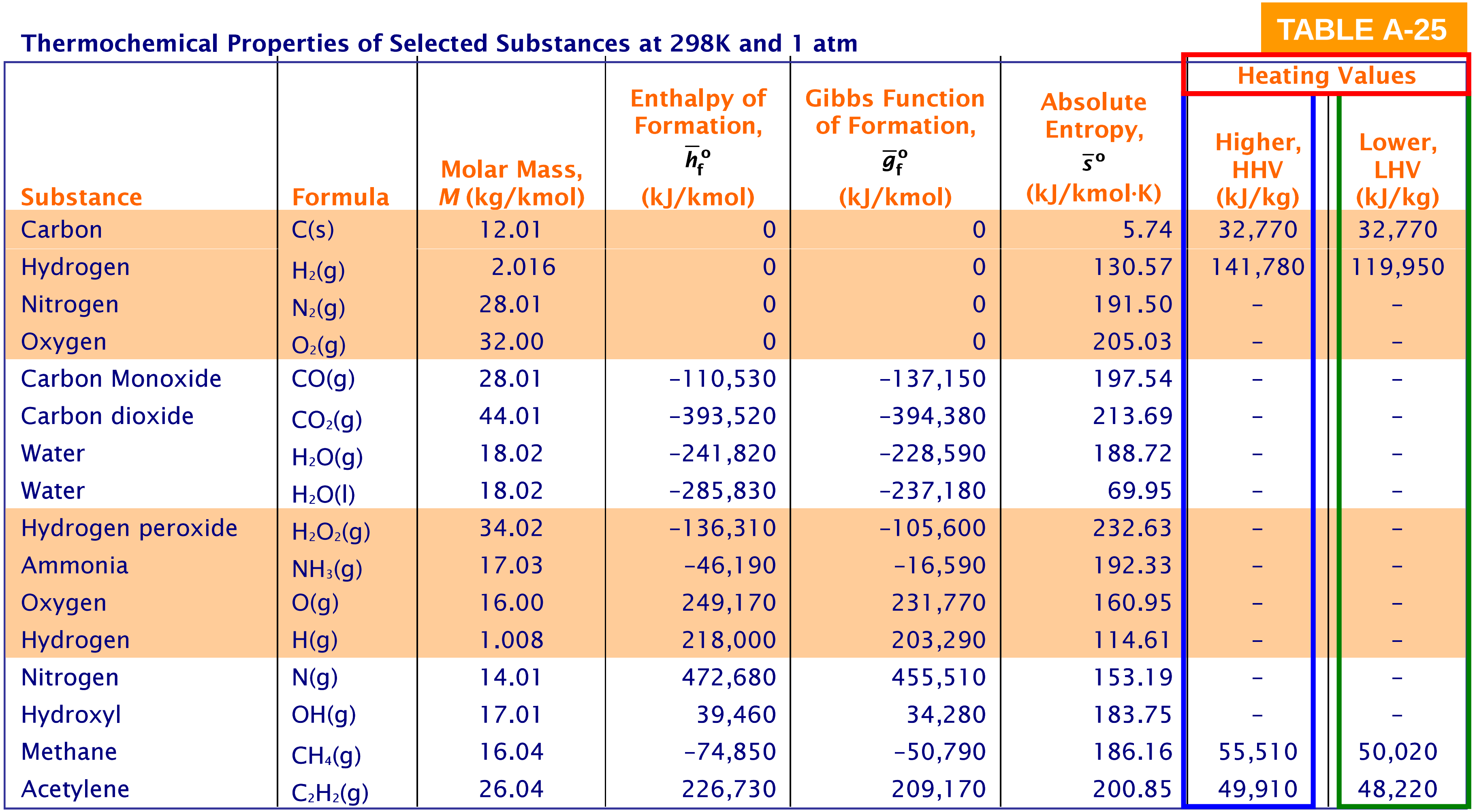


TABLE A-25

Thermochemical Properties of Selected Substances at 298K and 1 atm

Substance	Formula	Molar Mass, *M* (kg/kmol)	Enthalpy of Formation, $\bar{h}_f^o$ (kJ/kmol)	Gibbs Function of Formation, $\bar{g}_f^o$ (kJ/kmol)	Absolute Entropy, $\bar{s}^o$ (kJ/kmol·K)	Heating Values: Higher, HHV (kJ/kg)	Heating Values: Lower, LHV (kJ/kg)
Carbon	$C(s)$	12.01	0	0	5.74	32,770	32,770
Hydrogen	$H_2(g)$	2.016	0	0	130.57	141,780	119,950
Nitrogen	$N_2(g)$	28.01	0	0	191.50	–	–
Oxygen	$O_2(g)$	32.00	0	0	205.03	–	–
Carbon Monoxide	$CO(g)$	28.01	–110,530	–137,150	197.54	–	–
Carbon dioxide	$CO_2(g)$	44.01	–393,520	–394,380	213.69	–	–
Water	$H_2O(g)$	18.02	–241,820	–228,590	188.72	–	–
Water	$H_2O(l)$	18.02	–285,830	–237,180	69.95	–	–
Hydrogen peroxide	$H_2O_2(g)$	34.02	–136,310	–105,600	232.63	–	–
Ammonia	$NH_3(g)$	17.03	–46,190	–16,590	192.33	–	–
Oxygen	$O(g)$	16.00	249,170	231,770	160.95	–	–
Hydrogen	$H(g)$	1.008	218,000	203,290	114.61	–	–
Nitrogen	$N(g)$	14.01	472,680	455,510	153.19	–	–
Hydroxyl	$OH(g)$	17.01	39,460	34,280	183.75	–	–
Methane	$CH_4(g)$	16.04	–74,850	–50,790	186.16	55,510	50,020
Acetylene	$C_2H_2(g)$	26.04	226,730	209,170	200.85	49,910	48,220

Heating Values of Hydrocarbon Fuels

Example: Evaluate the lower heating value of liquid octane at **25ºC**, **1 atm**, in **kJ per kg of octane**, and compare with the value provided in Table A-25.

► The balanced chemical equation for complete combustion of octane is

$$C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O(g) + 47N_2$$

where all water formed is *assumed to be a vapor*.

Heating Values of Hydrocarbon Fuels

- ►With coefficients from the chemical equation, **Eq. (1)** reads

$$\begin{aligned}\overline{\mathrm{LHV}} = {} & 1\left(\bar{h}_f^o + \cancelto{0}{\Delta\bar{h}}\right)_{C_8H_{18}} + 12.5\left(\bar{h}_f^o + \cancelto{0}{\Delta\bar{h}}\right)_{O_2} + 47\left(\bar{h}_f^o + \cancelto{0}{\Delta\bar{h}}\right)_{N_2} \\ & - 8\left(\bar{h}_f^o + \cancelto{0}{\Delta\bar{h}}\right)_{CO_2} - 9\left(\bar{h}_f^o + \cancelto{0}{\Delta\bar{h}}\right)_{H_2O(g)} - 47\left(\bar{h}_f^o + \cancelto{0}{\Delta\bar{h}}\right)_{N_2}\end{aligned}$$

- ►Since the lower heating value at **25ºC** and **1 atm** is required, this reduces as follows

$$\begin{aligned}\overline{\mathrm{LHV}} = {} & 1\left(\bar{h}_f^o\right)_{C_8H_{18}} + 12.5\left(\bar{h}_f^o\right)_{O_2} + \cancel{47\left(\bar{h}_f^o\right)}_{N_2} \\ & - 8\left(\bar{h}_f^o\right)_{CO_2} - 9\left(\bar{h}_f^o\right)_{H_2O(g)} - \cancel{47\left(\bar{h}_f^o\right)}_{N_2}\end{aligned}$$

$$\overline{\mathrm{LHV}} = 1\left(\bar{h}_f^o\right)_{C_8H_{18}} + 12.5\left(\bar{h}_f^o\right)_{O_2} - 8\left(\bar{h}_f^o\right)_{CO_2} - 9\left(\bar{h}_f^o\right)_{H_2O(g)}$$

Heating Values of Hydrocarbon Fuels

▶With enthalpy of formation data obtained from Table A-25, we get the lower heating value on a per mole of octane basis.

$$\overline{\mathrm{LHV}} = -249{,}910\frac{\mathrm{kJ}}{\mathrm{kmol\,C_8H_{18}}} + 12.5\frac{\mathrm{kmol\,O_2}}{\mathrm{kmol\,C_8H_{18}}}\left(0\frac{\mathrm{kJ}}{\mathrm{kmol\,O_2}}\right)$$

$$-8\frac{\mathrm{kmol\,CO_2}}{\mathrm{kmol\,C_8H_{18}}}\left(-393{,}520\frac{\mathrm{kJ}}{\mathrm{kmol\,CO_2}}\right) - 9\frac{\mathrm{kmol\,H_2O}}{\mathrm{kmol\,C_8H_{18}}}\left(-241{,}820\frac{\mathrm{kJ}}{\mathrm{kmol\,H_2O}}\right)$$

$$\overline{\mathbf{LHV}} = \mathbf{5{,}074{,}630\ kJ/kmol\ C_8H_{18}}$$

Thermochemical Properties of Selected Substances at 298K and 1 atm

Substance	Formula	Molar Mass, *M* (kg/kmol)	Enthalpy of Formation, $\bar{h}_f^o$ (kJ/kmol)	Gibbs Function of Formation, $\bar{g}_f^o$ (kJ/kmol)	Absolute Entropy, $\bar{s}^o$ (kJ/kmol·K)	Heating Values	
						Higher, HHV (kJ/kg)	Lower, LHV (kJ/kg)
Carbon	C(s)	12.01	0	0	5.74	32,770	32,770
Hydrogen	H_2(g)	2.016	0	0	130.57	141,780	119,950
Nitrogen	N_2(g)	28.01	0	0	191.50	–	–
Oxygen	O_2(g)	32.00	0	0	205.03	–	–
Carbon Dioxide	CO_2(g)	44.01	–393,520	–394,380	213.69	–	–
Water	H_2O(g)	18.02	–241,820	–228,590	188.72	–	–
Water	H_2O(l)	18.02	–285,830	–237,180	69.95	–	–
Octane	C_8H_{18}(l)	114.22	–249,910	6,610	360.79	47,900	44,430

Heating Values of Hydrocarbon Fuels

► Dividing by the molecular weight of octane, the **lower heating value per kg of octane** is

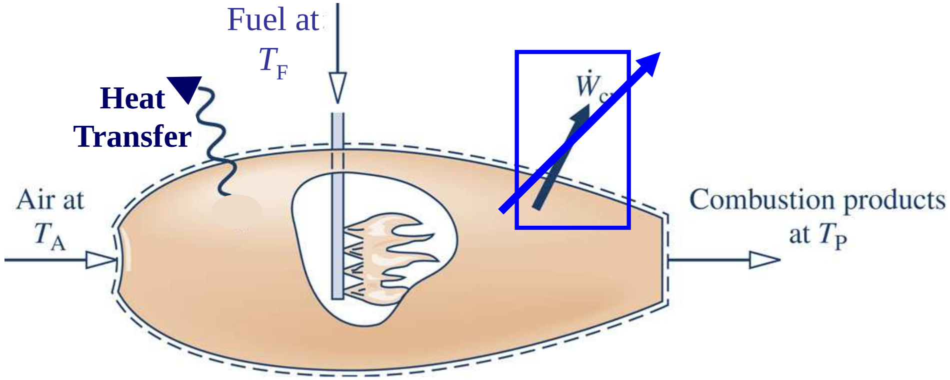
$$\mathrm{LHV} = \frac{5{,}074{,}630 \dfrac{\mathrm{kJ}}{\mathrm{kmol}\ \mathrm{C_8H_{18}}}}{114.22 \dfrac{\mathrm{kg}\ \mathrm{C_8H_{18}}}{\mathrm{kmol}\ \mathrm{C_8H_{18}}}}$$

$$\mathbf{LHV = 44{,}429\ kJ/kg\ C_8H_{18}}$$

► This value agrees with the value **(44,430 kJ/kg C_8H_{18})** from Table A-25, as expected.

Adiabatic Flame Temperature

- To introduce the adiabatic flame temperature concept, consider the reactor at steady state shown in the figure



- In the absence of work $\dot{W}_{cv}$ and appreciable kinetic and potential energy effects, the energy liberated on combustion is transferred from the reactor in two ways only
  - Energy accompanying the exiting combustion products
  - Heat transfer to the surroundings

Adiabatic Flame Temperature

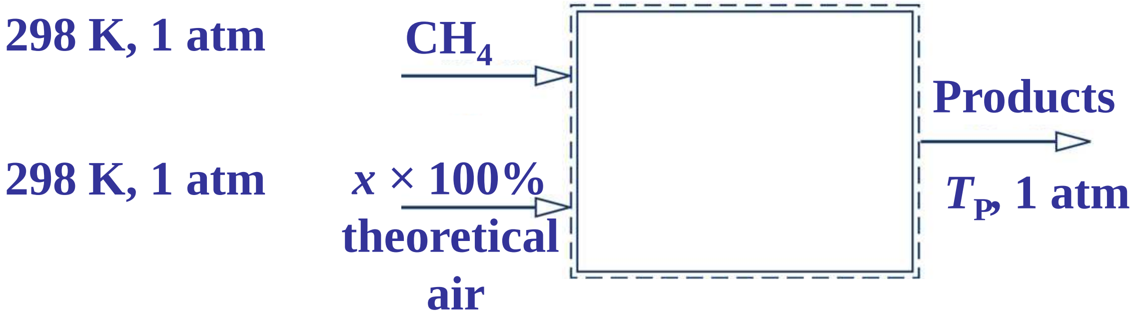
►The **smaller** the heat transfer to the surroundings, the **greater** the energy carried out with the combustion products and thus the **greater** the temperature T_P of the combustion products.

►The ***adiabatic flame temperature*** is the temperature that would be achieved by the products in the limit of ***adiabatic*** operation.

►The **maximum** adiabatic flame temperature corresponds to complete combustion with the theoretical amount of air.

Adiabatic Flame Temperature

Example: Methane gas at **25ºC**, **1 atm** enters an insulated reactor operating at steady state and burns completely with ***x*** × 100% of theoretical air entering at **25ºC**, **1 atm**. Plot the adiabatic flame temperature for ***x*** ranging from **1** to **4**. Assume ideal gas model principles apply.



Adiabatic Flame Temperature

- ►Complete combustion of CH_4 with the theoretical amount of air is

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

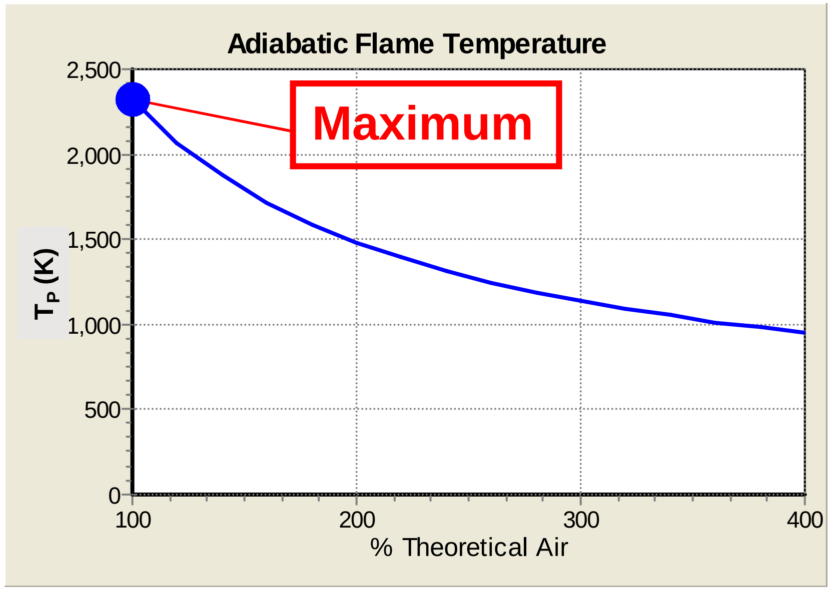
- ►Complete combustion of CH_4 with $x \times 100\%$ of the theoretical amount of air is

$$\boxed{CH_4 + 2x(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 2(x-1)O_2 + 7.52xN_2}$$

- ►For each specified value of x, the evaluation of adiabatic flame temperature requires an iterative solution of the corresponding energy rate balance.

Adiabatic Flame Temperature

- ►Applying an energy rate balance at steady state, using **Eq. 13.9** to express the enthalpy of each substance in terms of its enthalpy of formation, and varying x from **1** to **4** yields the plot at right.



- ►Once adequate oxygen has been provided to permit complete combustion, bringing in more air dilutes the combustion products, lowering their temperature.

Absolute Entropy

- For reacting systems, a common datum must be used to assign entropy values to participating substances. This is accomplished using the ***third law*** of thermodynamics.
- Based on empirical evidence, the third law states that the entropy of a pure crystalline substance is zero at the absolute zero of temperature, **0 K**.
- Values of entropy determined relative to this datum are called ***absolute entropy*** values.
- Observe that the ***steam tables*** and Tables A-7 through A-18 **DO NOT** provide absolute entropy values.

Absolute Entropy

►Table A-25 gives the value of the absolute entropy for selected substances at the standard state in units of kJ/kmol·K.

TABLE A-25

Thermochemical Properties of Selected Substances at 298K and 1 atm

Substance	Formula	Molar Mass, *M* (kg/kmol)	Enthalpy of Formation, $\overline{h}_f^o$ (kJ/kmol)	Gibbs Function of Formation, $\overline{g}_f^o$ (kJ/kmol)	Absolute Entropy, $\overline{s}^o$ (kJ/kmol·K)	Heating Values: Higher, HHV (kJ/kg)	Heating Values: Lower, LHV (kJ/kg)
Carbon	$C(s)$	12.01	0	0	5.74	32,770	32,770
Hydrogen	$H_2(g)$	2.016	0	0	130.57	141,780	119,950
Nitrogen	$N_2(g)$	28.01	0	0	191.50	–	–
Oxygen	$O_2(g)$	32.00	0	0	205.03	–	–
Carbon Monoxide	$CO(g)$	28.01	–110,530	–137,150	197.54	–	–
Carbon dioxide	$CO_2(g)$	44.01	–393,520	–394,380	213.69	–	–
Water	$H_2O(g)$	18.02	–241,820	–228,590	188.72	–	–
Water	$H_2O(l)$	18.02	–285,830	–237,180	69.95	–	–
Hydrogen peroxide	$H_2O_2(g)$	34.02	–136,310	–105,600	232.63	–	–
Ammonia	$NH_3(g)$	17.03	–46,190	–16,590	192.33	–	–
Oxygen	$O(g)$	16.00	249,170	231,770	160.95	–	–
Hydrogen	$H(g)$	1.008	218,000	203,290	114.61	–	–
Nitrogen	$N(g)$	14.01	472,680	455,510	153.19	–	–
Hydroxyl	$OH(g)$	17.01	39,460	34,280	183.75	–	–
Methane	$CH_4(g)$	16.04	–74,850	–50,790	186.16	55,510	50,020
Acetylene	$C_2H_2(g)$	26.04	226,730	209,170	200.85	49,910	48,220

Absolute Entropy

- ►Table A-23 gives the value of the absolute entropy for selected substances versus temperature at a pressure of **1 atm** in units of kJ/kmol·K. In these tables
  - ►The absolute entropy at **1 atm** and temperature ***T*** is designated $s^o(T)$.
  - ►The ideal-gas model applies to the gases.

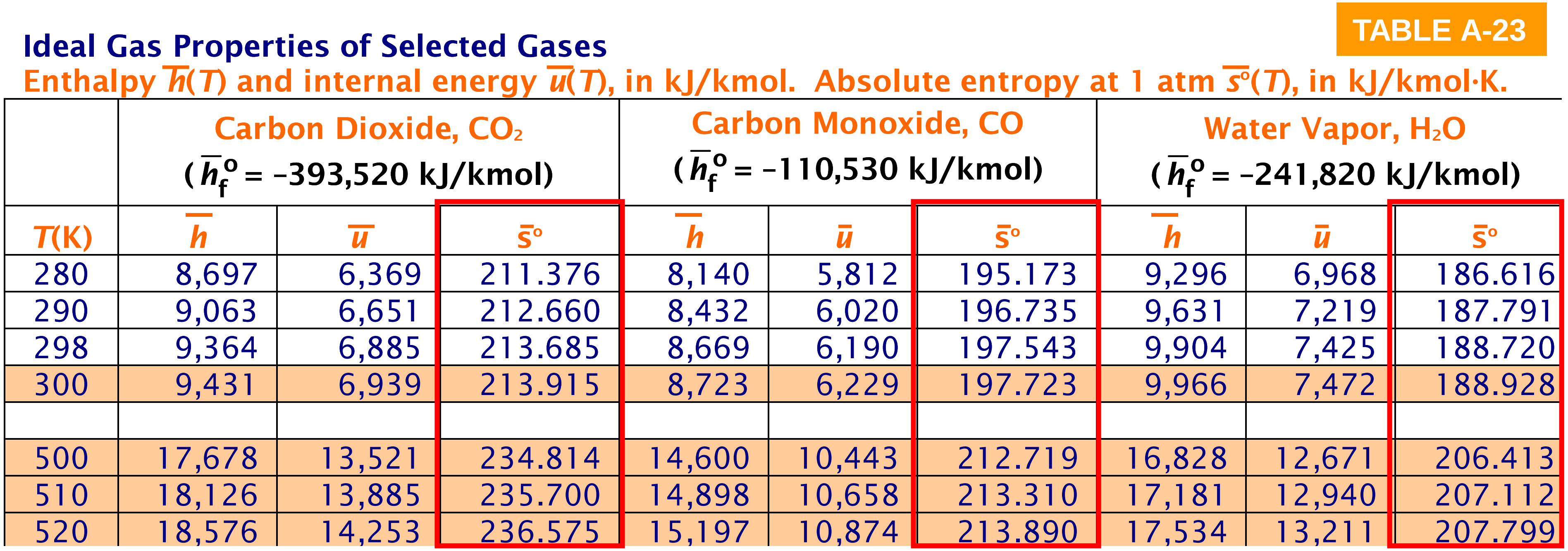


TABLE A-23

Ideal Gas Properties of Selected Gases

Enthalpy $\bar{h}(T)$ and internal energy $\bar{u}(T)$, in kJ/kmol. Absolute entropy at 1 atm $\bar{s}^o(T)$, in kJ/kmol·K.

	Carbon Dioxide, CO_2 ($\bar{h}_f^o$ = –393,520 kJ/kmol)			Carbon Monoxide, CO ($\bar{h}_f^o$ = –110,530 kJ/kmol)			Water Vapor, H_2O ($\bar{h}_f^o$ = –241,820 kJ/kmol)		
T(K)	$\bar{h}$	$\bar{u}$	$\bar{s}^o$	$\bar{h}$	$\bar{u}$	$\bar{s}^o$	$\bar{h}$	$\bar{u}$	$\bar{s}^o$
280	8,697	6,369	211.376	8,140	5,812	195.173	9,296	6,968	186.616
290	9,063	6,651	212.660	8,432	6,020	196.735	9,631	7,219	187.791
298	9,364	6,885	213.685	8,669	6,190	197.543	9,904	7,425	188.720
300	9,431	6,939	213.915	8,723	6,229	197.723	9,966	7,472	188.928
500	17,678	13,521	234.814	14,600	10,443	212.719	16,828	12,671	206.413
510	18,126	13,885	235.700	14,898	10,658	213.310	17,181	12,940	207.112
520	18,576	14,253	236.575	15,197	10,874	213.890	17,534	13,211	207.799

Absolute Entropy

►For the ideal gases in Table A-23, the absolute entropy at a state where temperature is T and pressure is p is given by

$$\bar{s}(T, p) = \bar{s}^\circ(T) - \bar{R} \ln \frac{p}{p_{\text{ref}}} \qquad \text{(ideal gas)}$$

(Eq. 13.22)

The first term on the right is the absolute entropy at temperature T and pressure p_{ref} **= 1 atm**.

Absolute Entropy

►For the ***i*^th^** component of an ideal gas mixture, **Eq. 13.22** takes the form

$$\bar{s}_i(T, p_i) = \bar{s}_i^{\circ}(T) - \bar{R} \ln \frac{y_i p}{p_{\text{ref}}} \qquad \left(\begin{array}{c}\text{component } i \text{ of an} \\ \text{ideal gas mixture}\end{array}\right)$$

(Eq. 13.23)

In this expression, p_i is the partial pressure of component ***i***, y_i is the mole fraction of component ***i***, and p is the mixture pressure.

Absolute Entropy

Example: Applying **Eq. 13.23**, evaluate the absolute entropy for dry air at $\boldsymbol{T}$ **= 350 K**, $\boldsymbol{p}$ **= 2 atm**, in kJ/kmol(air)·K. The molar analysis is

$$\boxed{\begin{array}{l} y_{O_2} = \mathbf{0.21\ kmol\ (O_2)/kmol(air)} \\ y_{N_2} = \mathbf{0.79\ kmol(N_2)/kmol(air)} \end{array}}$$

and the ideal gas model applies.

Absolute Entropy

- ▶With data from Table A-23, **Eq. 13.23** gives

$$\bar{s}_{O_2} = \bar{s}^{o}_{O_2} - \bar{R}\ln\left(\frac{y_{O_2}p}{p_{\text{ref}}}\right)$$

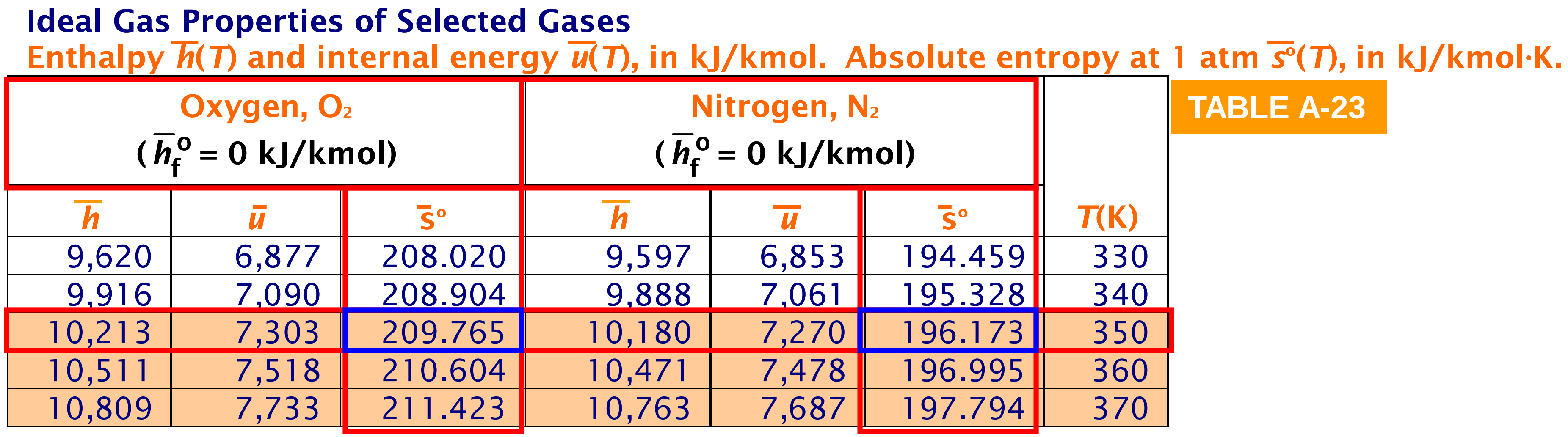
$$\bar{s}_{N_2} = \bar{s}^{o}_{N_2} - \bar{R}\ln\left(\frac{y_{N_2}p}{p_{\text{ref}}}\right)$$

$$\bar{s}_{O_2} = 209.765 - 8.314\ln\left(\frac{(0.21)2\text{ atm}}{1\text{ atm}}\right)$$

$$\bar{s}_{N_2} = 196.173 - 8.314\ln\left(\frac{(0.79)2\text{ atm}}{1\text{ atm}}\right)$$

$$\boxed{\bar{s}_{O_2} = \mathbf{216.977\ kJ/kmol(O_2)\cdot K}}$$

$$\boxed{\bar{s}_{N_2} = \mathbf{192.370\ kJ/kmol(N_2)\cdot K}}$$



Ideal Gas Properties of Selected Gases

Enthalpy $\bar{h}(T)$ and internal energy $\bar{u}(T)$, in kJ/kmol. Absolute entropy at 1 atm $\bar{s}^{o}(T)$, in kJ/kmol·K.

TABLE A-23

Oxygen, O_2 ($\bar{h}^{o}_{f}$ = 0 kJ/kmol)			Nitrogen, N_2 ($\bar{h}^{o}_{f}$ = 0 kJ/kmol)			
$\bar{h}$	$\bar{u}$	$\bar{s}^{o}$	$\bar{h}$	$\bar{u}$	$\bar{s}^{o}$	T(K)
9,620	6,877	208.020	9,597	6,853	194.459	330
9,916	7,090	208.904	9,888	7,061	195.328	340
10,213	7,303	209.765	10,180	7,270	196.173	350
10,511	7,518	210.604	10,471	7,478	196.995	360
10,809	7,733	211.423	10,763	7,687	197.794	370

Absolute Entropy

- Finally, per kmol of air

$$\bar{s} = \left(0.21\frac{\text{kmol}(\text{O}_2)}{\text{kmol(air)}}\right)\left(216.977\frac{\text{kJ}}{\text{kmol}(\text{O}_2)\cdot K}\right) + \left(0.79\frac{\text{kmol}(\text{N}_2)}{\text{kmol(air)}}\right)\left(192.370\frac{\text{kJ}}{\text{kmol}(\text{N}_2)\cdot K}\right)$$

$$\boxed{\bar{s} = \mathbf{197.537\ kJ/kmol(air)\cdot K}}$$

Evaluating Gibbs Function for Reacting Systems

► The ***specific Gibbs function*** $\bar{g}$ is given by

$$\bar{g} = \bar{h} - T\bar{s} \qquad \text{(Eq. 13.27)}$$

► Gibbs function is a property because it is defined in terms of other properties.

► Gibbs function has no physical significance – in general, but contributes to the development of chemical exergy in the next part of Chapter 13, and has other important applications.

Evaluating Gibbs Function for Reacting Systems

►As for enthalpy, a Gibbs function datum for the study of reacting systems is established by assigning a value of zero to the Gibbs function of $\mathbf{C}$, $\mathbf{H}_2$, $\mathbf{N}_2$, $\mathbf{O}_2$ at the standard reference state: **298.15 K**, **1 atm**.

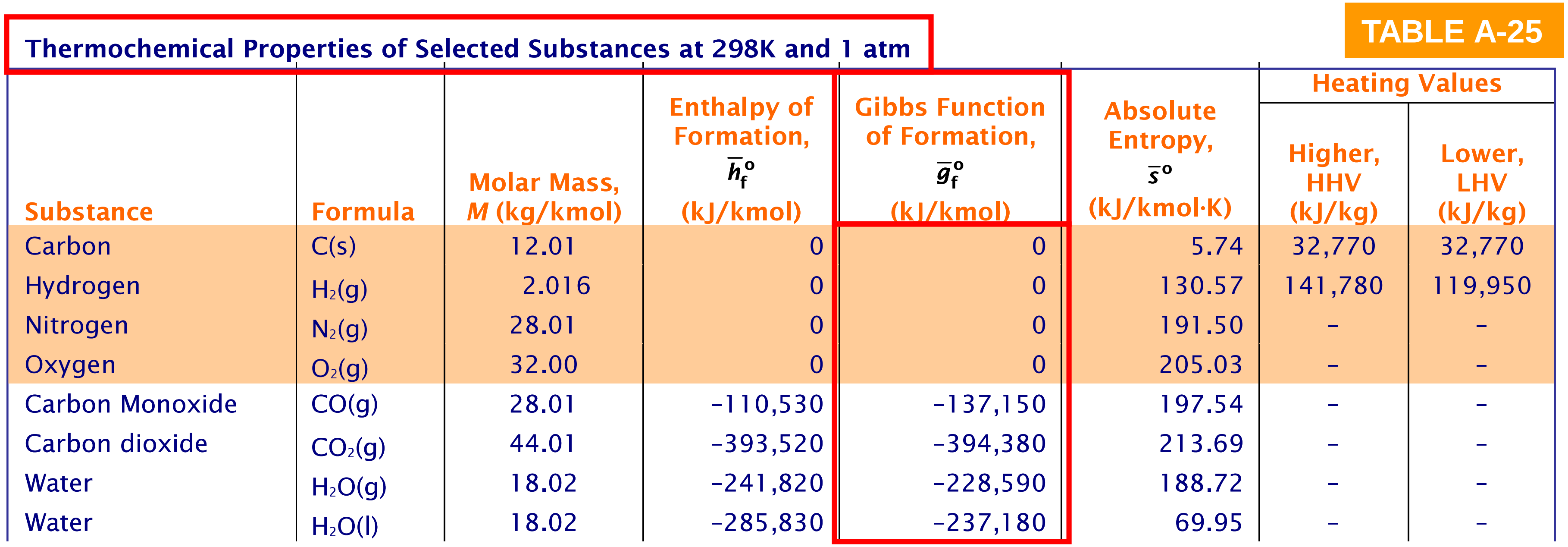
►The Gibbs function of a ***compound*** at the standard state equals its ***Gibbs function of formation***, denoted $\bar{g}_{\mathrm{f}}^{\mathrm{o}}$.

►The Gibbs function of formation is the change in the Gibbs function for the reaction in which the compound is formed from its elements, the compound and elements all being at the standard state.

Evaluating Gibbs Function for Reacting Systems

►Table A-25 gives values of the Gibbs function of formation in kJ/kmol.

►As indicated by the table heading these data apply only to the standard state, **298 K**, **1 atm**.



Thermochemical Properties of Selected Substances at 298K and 1 atm

TABLE A-25

Substance	Formula	Molar Mass, *M* (kg/kmol)	Enthalpy of Formation, $\bar{h}_f^o$ (kJ/kmol)	Gibbs Function of Formation, $\bar{g}_f^o$ (kJ/kmol)	Absolute Entropy, $\bar{s}^o$ (kJ/kmol·K)	Heating Values	
						Higher, HHV (kJ/kg)	Lower, LHV (kJ/kg)
Carbon	$C(s)$	12.01	0	0	5.74	32,770	32,770
Hydrogen	$H_2(g)$	2.016	0	0	130.57	141,780	119,950
Nitrogen	$N_2(g)$	28.01	0	0	191.50	–	–
Oxygen	$O_2(g)$	32.00	0	0	205.03	–	–
Carbon Monoxide	$CO(g)$	28.01	-110,530	-137,150	197.54	–	–
Carbon dioxide	$CO_2(g)$	44.01	-393,520	-394,380	213.69	–	–
Water	$H_2O(g)$	18.02	-241,820	-228,590	188.72	–	–
Water	$H_2O(l)$	18.02	-285,830	-237,180	69.95	–	–

Evaluating Gibbs Function for Reacting Systems

►The specific Gibbs function of a compound at a state where temperature is ***T*** and pressure is ***p*** is determined from

$$\bar{g}(T,p) = \bar{g}_f^\circ + [\bar{g}(T,p) - \bar{g}(T_{\text{ref}}, p_{\text{ref}})] = \bar{g}_f^\circ + \Delta\bar{g}$$

(Eq. 13.28a)

where

$$\Delta\bar{g} = [\bar{h}(T,p) - \bar{h}(T_{\text{ref}}, p_{\text{ref}})] - [T\bar{s}\,(T,p) - T_{\text{ref}}\,\bar{s}(T_{\text{ref}}, p_{\text{ref}})]$$

(Eq. 13.28b)