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.

Exergy Analysis

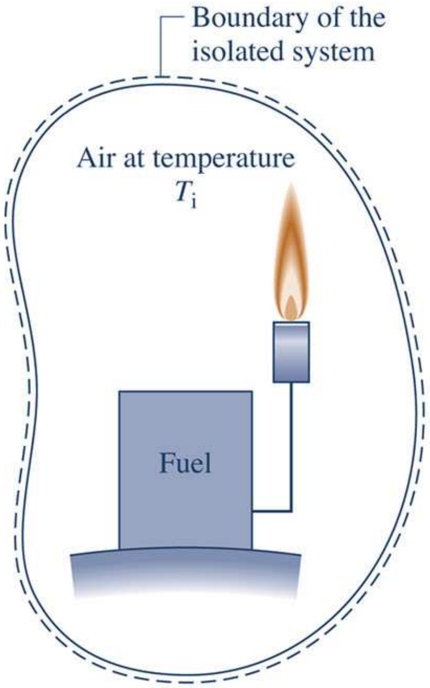
►**Exergy analysis** contributes to the goal of making more effective use of nonrenewable energy resources: natural gas, coal, and oil, by determining the locations, types, and true magnitudes of waste and loss in systems fueled by such resources.

►**Exergy analysis** is also relevant for designing more effective thermal systems of all types, guiding efforts to reduce inefficiencies in such systems, and evaluating system economics.

Reviewing Exergy Concepts

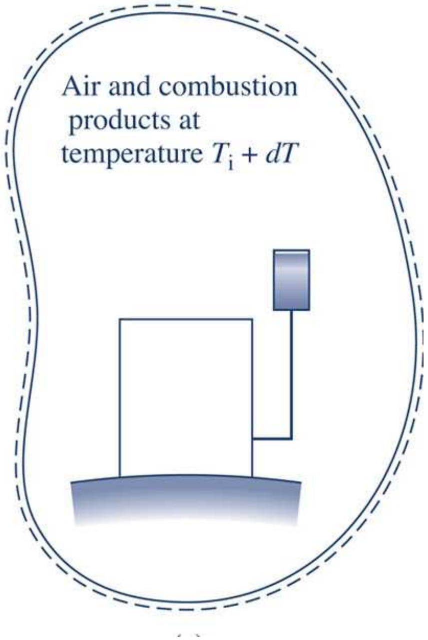
►When you fill an automobile's fuel tank with gasoline, it is the exergy of the gasoline you seek and for which you pay.

►Exergy is not just another aspect of energy. Exergy and energy are related but distinctly different quantities. These differences are explored with the figure at right, which shows an isolated system consisting initially of a small container of fuel surrounded by air in abundance.



Reviewing Exergy Concepts

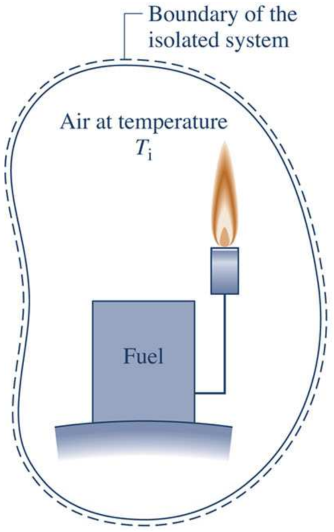
- ►Suppose the fuel burns so finally there is a slightly warm mixture of air and the combustion products formed.
  - ►Since air is abundantly present, the temperature of the final mixture is nearly the same as the initial air temperature.
  - ►The total ***quantity*** of energy associated with the system is ***constant*** because no energy transfers take place across the boundary of an isolated system and, by the first law of thermodynamics, energy is conserved.

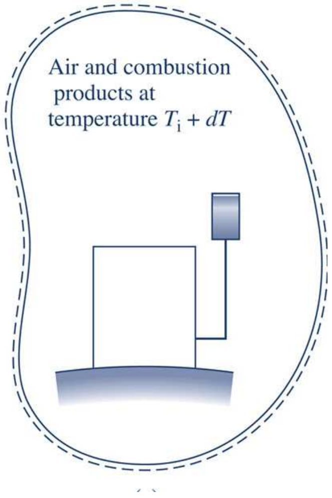


Reviewing Exergy Concepts

►The initial fuel-air combination has a much greater ***potential for use*** than the final warm mixture. For instance, the fuel might be used to generate electricity, produce steam, or power a car whereas the final warm mixture is clearly unsuited for such applications.

►In fact, during the process shown in the figures the initial potential for use is predominately ***destroyed*** owing to the irreversible nature of that process.

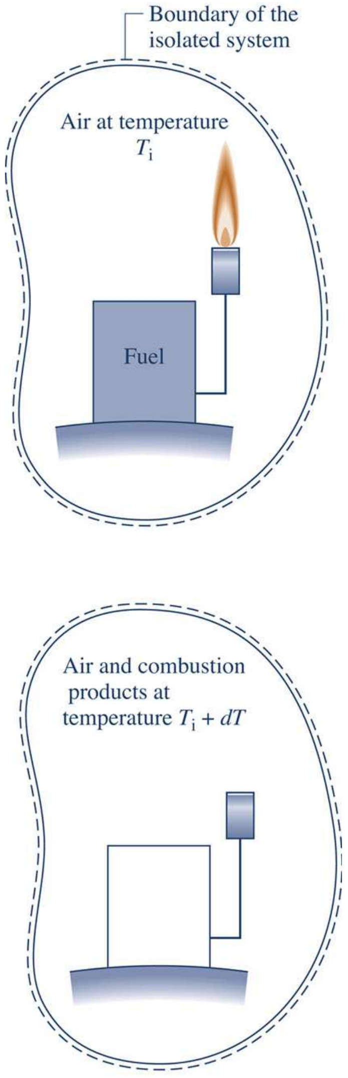




Reviewing Exergy Concepts

►The fuel present initially also has economic value, but economic value diminishes as fuel is consumed. The final warm mixture has negligible economic value.

►Exergy is the property that quantifies the ***potential for use*** and it is exergy that has economic value.



Reviewing Exergy Concepts

►Exergy is the ***maximum*** theoretical work obtainable from an overall system of system plus ***exergy reference environment*** as the system passes from a specified state to equilibrium with the environment.

In this definition, exergy reference environment refers to a thermodynamic model for the Earth and its atmosphere.

►If temperature and/or pressure of a system differ from that of the environment, the system has exergy. More precisely, the system has a ***thermomechanical*** contribution to its exergy. This contribution suffices for the applications of Chapter 7. Another contribution – chemical exergy – arises when there is a composition difference between the system and environment. Chemical exergy is the focus of our present study of exergy.

Reviewing Exergy Concepts

►For conceptual and computational ease, we think of the system passing to equilibrium with the environment in two steps. With this approach, exergy is the sum of two contributions: the thermomechanical and the chemical. Thus on a unit mass basis, the ***total exergy*** is

$$\mathrm{e} = \underline{(u - u_0) + p_0(v - v_0) - T_0(s - s_0) + \frac{\mathrm{V}^2}{2} + gz} + \mathrm{e}^{\mathrm{ch}}$$

(Eq. 13.46)

where the underlined term is the thermomechanical contribution **(Eq. 7.2)** and e^{ch} is the chemical contribution.

Reviewing Exergy Concepts

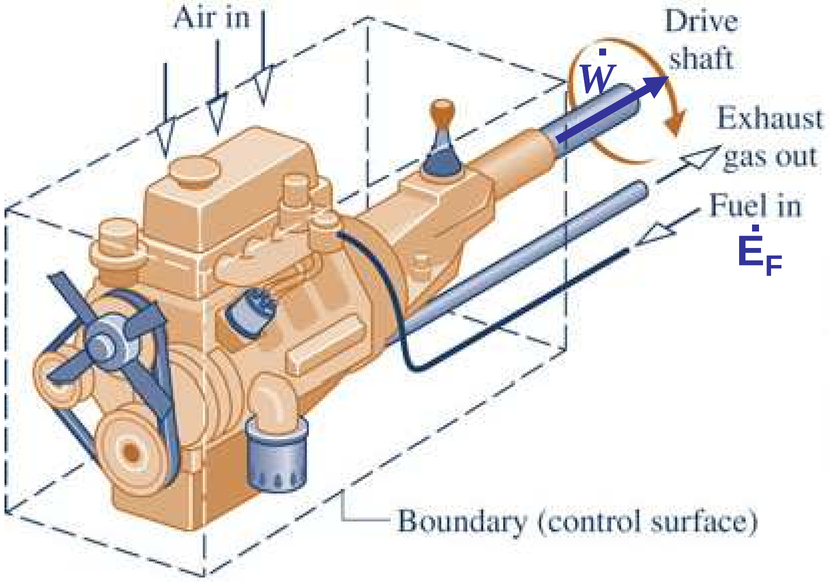
►Similarly, the ***total flow exergy*** at an inlet or exit of a control volume is

$$\mathrm{e_f} = \underline{h - h_0 - T_0(s - s_0) + \frac{V^2}{2} + gz} + \mathrm{e}^{\mathrm{ch}}$$ **(Eq. 13.47)**

where the underlined term is the thermomechanical contribution **(Eq. 7.14)** and e^{ch} is the chemical contribution.

Exergetic Efficiency of an Engine

► An exergy accounting for the engine at steady-state reads:



► **Exergy in**:

- **Fuel**, $\dot{E}_F$ (predominately chemical exergy)
- **Combustion air** (typically negligible when coming directly from the ambient)

► **Exergy out**:

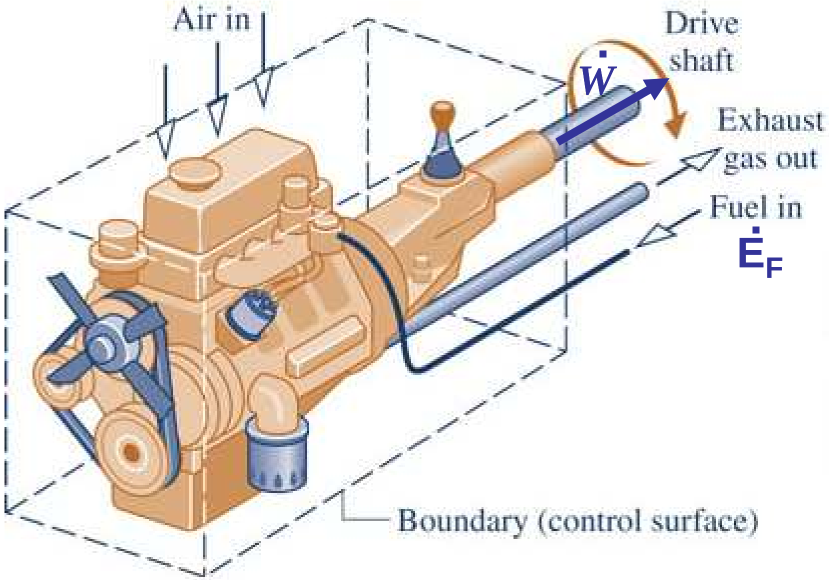
- **Power developed**, $\dot{W}$
- **Combustion products** (thermomechanical and chemical exergy)
- **Accompanying stray heat transfer** to the surroundings

► **Exergy destroyed within the engine**: (predominately exergy destroyed during combustion)

Exergetic Efficiency of an Engine

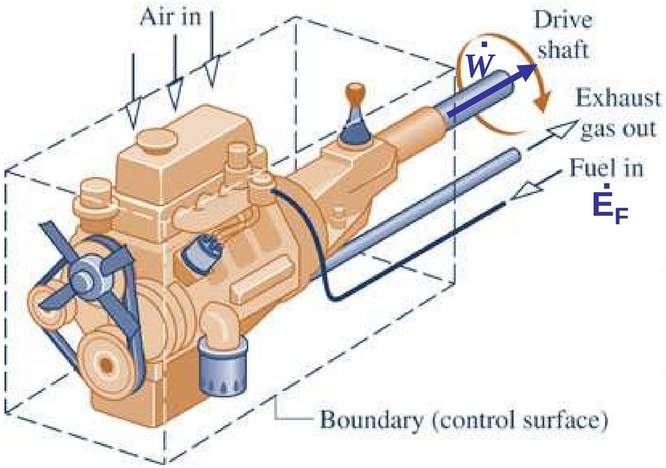
►If the exergy carried out with the combustion products and stray heat transfer are regarded as losses, an ***exergetic efficiency*** gauging the extent to which the exergy of the fuel is converted to power is

$$\varepsilon = \frac{\dot{W}}{\dot{E}_F} \qquad \textbf{(1)}$$



Exergetic Efficiency of an Engine

►**Example**: An internal combustion engine develops **50 hp** for a fuel input of **1.98×10^{-3} kg/s**. If the exergy of the fuel is **47,000 kJ/kg**, evaluate the exergetic efficiency given by **Eq. (1)**.



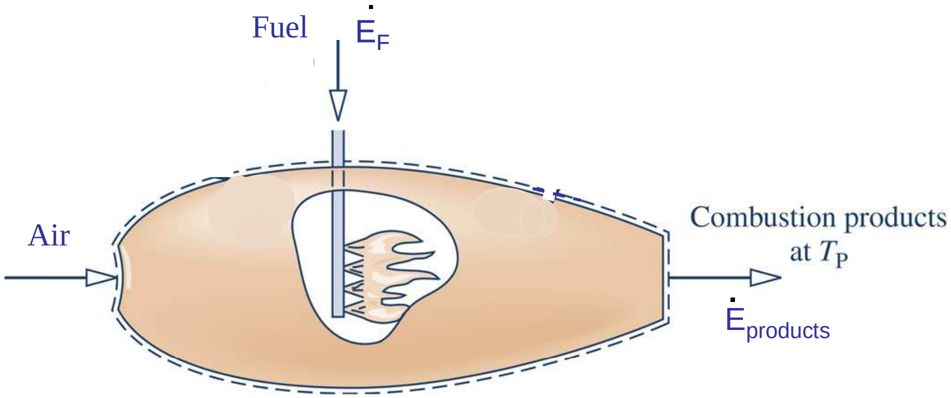
Inserting values

$$\varepsilon = \frac{50\ \text{hp}}{\left(1.98\times10^{-3}\ \dfrac{\text{kg}}{\text{s}}\right)\left(47{,}000\ \dfrac{\text{kJ}}{\text{kg}}\right)}\left|\frac{0.7457\ \dfrac{\text{kJ}}{\text{s}}}{1\ \text{hp}}\right|$$

$$\boxed{\varepsilon = \mathbf{0.40\ (40\%)}}$$

Exergetic Efficiency of a Reactor

►An exergy accounting for the reactor at steady-state reads:



- ►**Exergy in**:
  - ● **Fuel**, $\dot{E}_F$ (predominately chemical exergy)
  - ● **Combustion air** (typically negligible when coming directly from the ambient)
- ►**Exergy out**:
  - ●**Combustion products**, $\dot{E}_{products}$ (thermomechanical and chemical exergy)
  - ● **Accompanying stray heat transfer** to the surroundings
- ►**Exergy destroyed within the reactor**: (predominately exergy destroyed during combustion)

Exergetic Efficiency of a Reactor

►Regarding the exergy carried out with stray heat transfer as a loss, an ***exergetic efficiency*** for the reactor is

$$\varepsilon = \frac{\dot{E}_{\text{products}}}{\dot{E}_{F}}$$

►For the reactor of **Example 13.16**,

- ε **= 70.3%** when there is complete combustion with the theoretical amount of air.
- ε **= 46.3%** when there is complete combustion with 400% of the theoretical amount of air.

Note that excess air dilutes the combustion products, lowering the temperature of the products and thus the exergy of the products.

Evaluating Chemical Exergy

- ►To evaluate chemical exergy values, the first step is to specify the ***exergy reference environment*** – that is, to model appropriately the Earth and its atmosphere.
- ►Modeling considerations include
  - ►Specifying the environmental temperature T_0 and pressure p_0.
  - ►Specifying a set of reference substances with concentrations closely corresponding to the chemical makeup of the natural environment.

Evaluating Chemical Exergy

- ►Reference substances may include
  - ►Gaseous components of the atmosphere: N_2, O_2, CO_2, $H_2O(g)$, and other gases.
  - ►Solid substances from the Earth's crust.
  - ►Substances from the oceans.
- ►At one extreme, such considerations lead to tables of "standard" chemical exergy values that stem from painstaking modeling programs. At the other extreme, relatively elementary modeling provides chemical exergy values useful for at least preliminary engineering analysis.

Standard Chemical Exergy

►Standard molar chemical exergy values of selected substances, in kJ/kmol, are provided in Table A-26, together with a brief description of the underlying rationale for each of the two models employed.

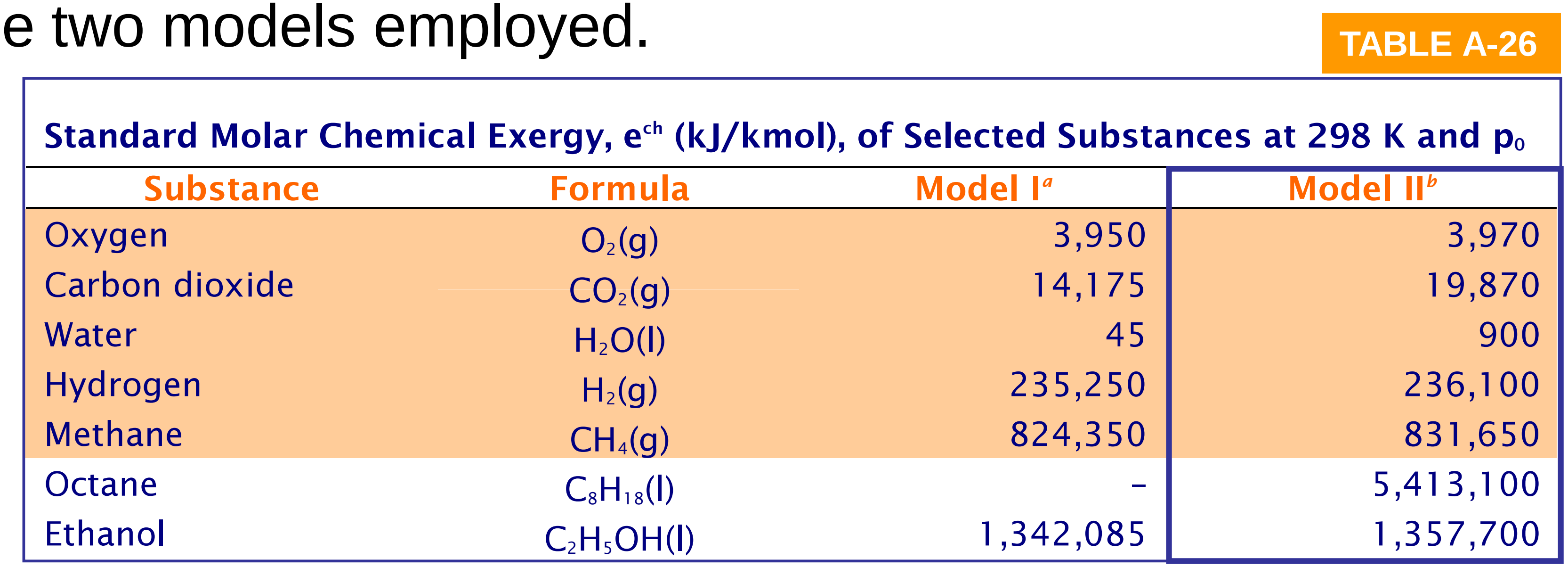


TABLE A-26

Standard Molar Chemical Exergy, e^{ch} (kJ/kmol), of Selected Substances at 298 K and p_0

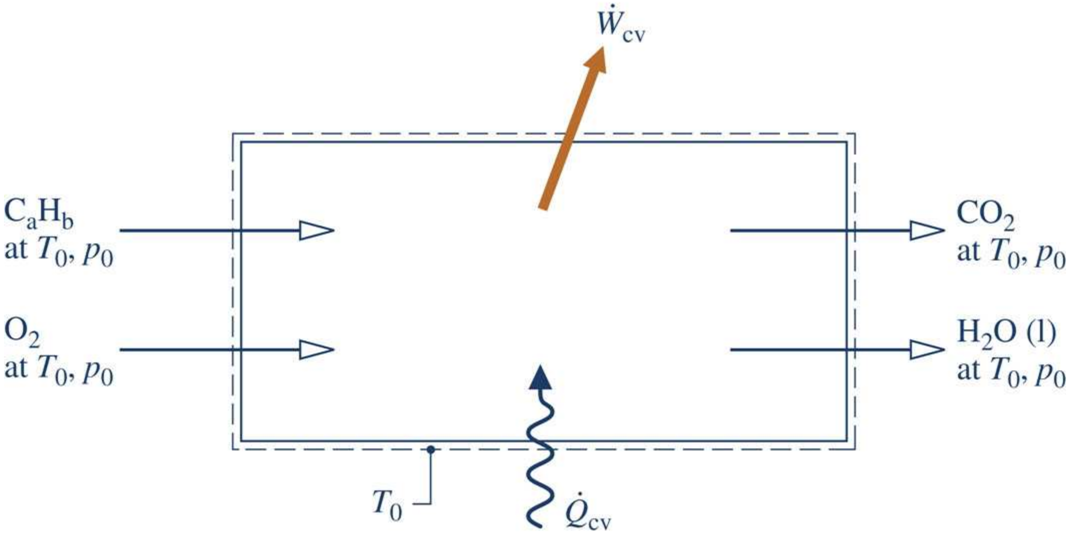
Substance	Formula	Model I[a]	Model II[b]
Oxygen	$O_2(g)$	3,950	3,970
Carbon dioxide	$CO_2(g)$	14,175	19,870
Water	$H_2O(l)$	45	900
Hydrogen	$H_2(g)$	235,250	236,100
Methane	$CH_4(g)$	824,350	831,650
Octane	$C_8H_{18}(l)$	–	5,413,100
Ethanol	$C_2H_5OH(l)$	1,342,085	1,357,700

►Model II, or variations of it, is commonly used in practice. Model I is provided only to show for comparison the result of an alternative modeling effort. Despite differences in modeling approach there is acceptable agreement between the two sets of data.

Standard Chemical Exergy

- ►In most cases the value of the standard chemical exergy can be obtained from the engineering literature. Still, in principle, if the value of the standard chemical exergy of a substance is unknown, it can be evaluated by considering a reaction of that substance with other substances for which the standard chemical exergy values are known.

- ►To illustrate, consider the figure where a hydrocarbon $\mathbf{C_aH_b}$ reacts completely with $\mathbf{O_2}$ to form $\mathbf{CO_2}$ and $\mathbf{H_2O(l)}$, each substance at T_0, p_0.



$$C_aH_b + \left(a + \frac{b}{4}\right)O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O(l)$$

Standard Chemical Exergy

►Applying energy, entropy, and exergy balances, and representing the result in terms of Gibbs functions for computational ease, the standard chemical exergy of C_aH_b is

$$\bar{e}^{ch}_{F} = \boxed{\left[\bar{g}_F + \left(a + \frac{b}{4}\right)\bar{g}_{O_2} - a\bar{g}_{CO_2} - \frac{b}{2}\bar{g}_{H_2O(l)}\right](T_0, p_0)} \\ \underline{+\, a\bar{e}^{ch}_{CO_2} + \left(\frac{b}{2}\right)\bar{e}^{ch}_{H_2O(l)} - \left(a + \frac{b}{4}\right)\bar{e}^{ch}_{O_2}}$$

(Eq. 13.44b)

where **F** denotes the substance represented by C_aH_b

►The first term on the right involves the Gibbs function at T_0, p_0 of each substance appearing in the reaction equation. The coefficient of each of these Gibbs function terms corresponds to its coefficient in the reaction equation.

►As shown by the underlined term of this expression, the only standard chemical exergy data required is for CO_2, $H_2O(l)$, and O_2. Each of these terms has the same coefficient as in the reaction equation.

Standard Chemical Exergy

Example: Consider an application of **Eq. 13.44b** to the case of hydrogen, **H_2**, when **T_0 = 298.15 K (25°C)**, **p_0 = 1 atm**. For this application we can use Gibbs function data directly from Table A-25 and standard chemical exergies from Table A-26 (Model II), since each source corresponds to **298.15 K, 1 atm**.

▶ Here **a = 0**, **b = 2** and the reaction underlying **Eq. 13.44b**

$$C_aH_b + \left(a + \frac{b}{4}\right)O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O(l)$$

reduces to read $\boxed{\mathbf{H_2 + 0.5O_2 \rightarrow H_2O(l)}}$

▶ **Equation 13.44b** reduces to

$$\bar{e}_F^{ch} = \left[\bar{g}_F + 0.5\bar{g}_{O_2} - \bar{g}_{H_2O(l)}\right](T_0,\ p_0) + \bar{e}_{H_2O(l)}^{ch} - 0.5\bar{e}_{O_2}^{ch} \qquad \mathbf{(1)}$$

Standard Chemical Exergy

- ▶ From Table A-25 we get

$$\bar{g}^{o}_{f,H_2} = 0 \text{ kJ/kmol} \qquad \bar{g}^{o}_{f,O_2} = 0 \text{ kJ/kmol}$$

$$\bar{g}^{o}_{f,H_2O} = -237{,}180 \text{ kJ/kmol}$$

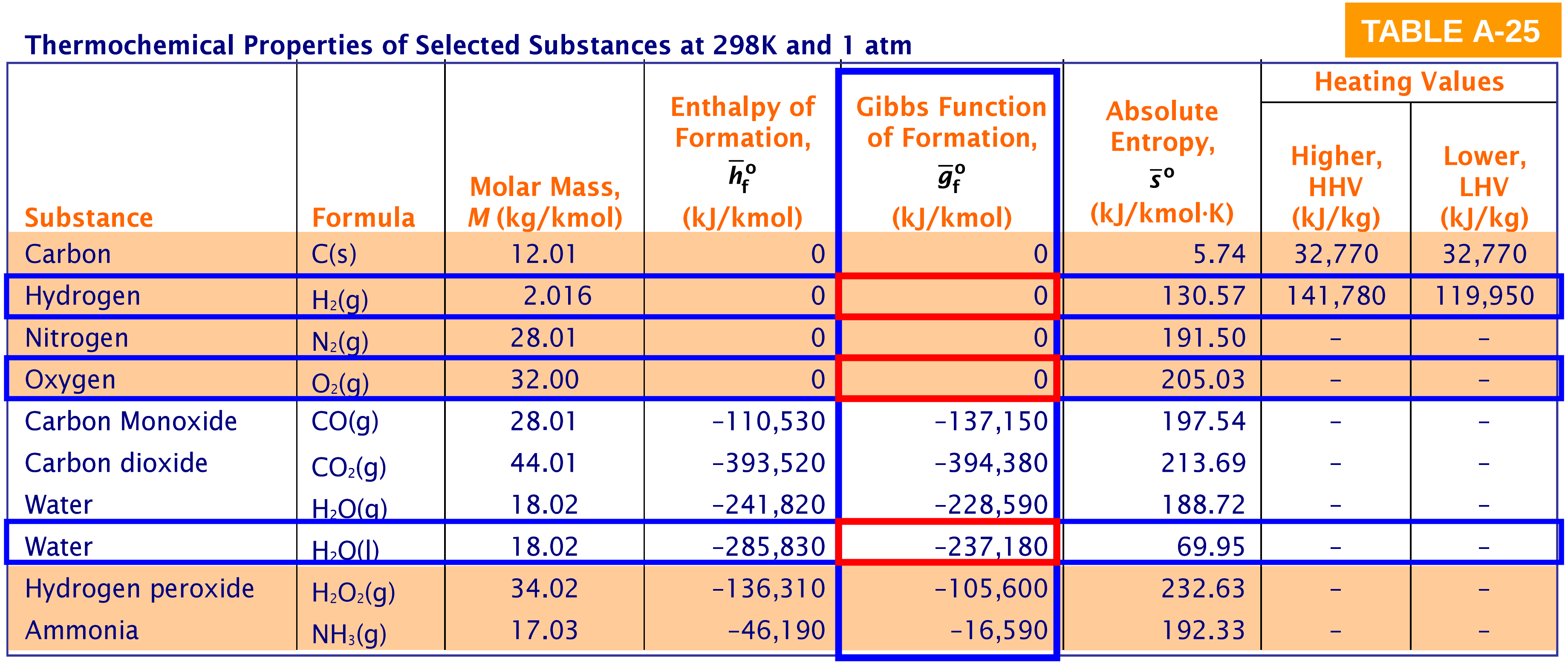


TABLE A-25

Thermochemical Properties of Selected Substances at 298K and 1 atm

Substance	Formula	Molar Mass, *M* (kg/kmol)	Enthalpy of Formation, $\bar{h}^o_f$ (kJ/kmol)	Gibbs Function of Formation, $\bar{g}^o_f$ (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	–	–

Standard Chemical Exergy

- From Table A-26 **(Model II)** we get

$$\bar{e}^{ch}_{O_2} = 3{,}970\ \mathrm{kJ/kmol}$$

$$\bar{e}^{ch}_{H_2O} = 900\ \mathrm{kJ/kmol}$$

TABLE A-26

Standard Molar Chemical Exergy, e^{ch} (kJ/kmol), of Selected Substances at 298 K and p_0

Substance	Formula	Model I[a]	Model II[b]
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Hydrogen	$H_2(g)$	235,250	236,100
Methane	$CH_4(g)$	824,350	831,650
Octane	$C_8H_{18}(l)$	–	5,413,100
Ethanol	$C_2H_5OH(l)$	1,342,085	1,357,700

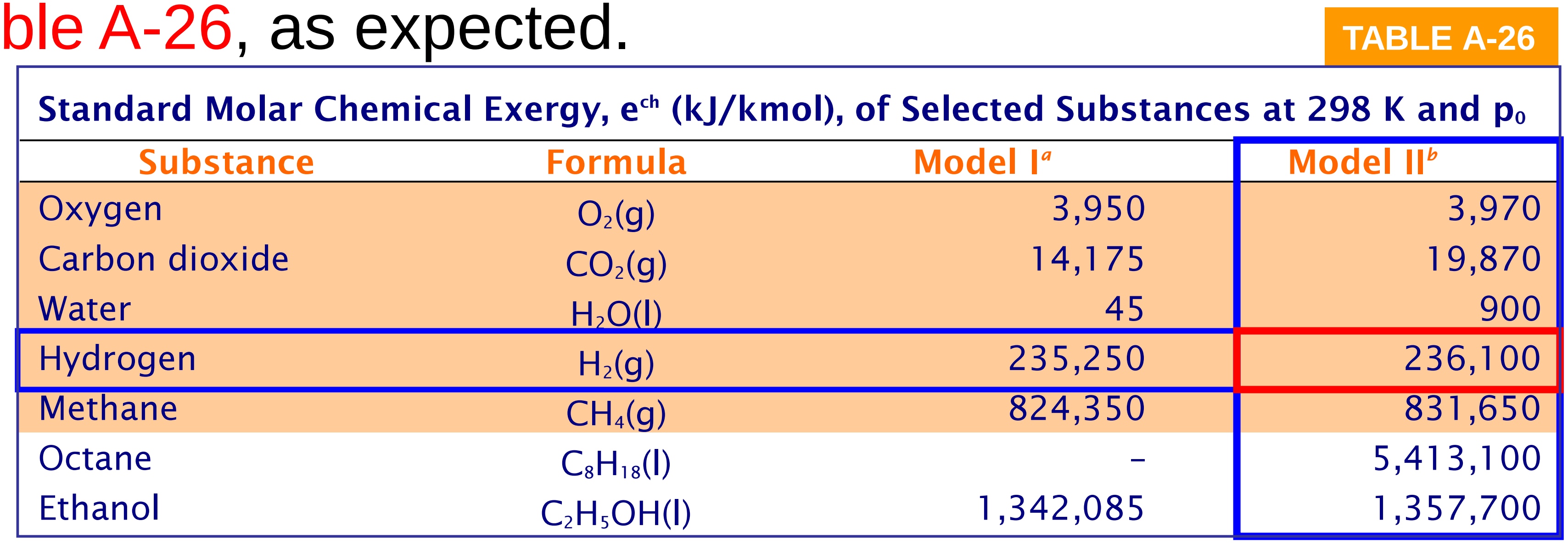
Standard Chemical Exergy

- ► Substituting values in **Eq. (1)**

$$\bar{e}^{ch}_{H_2} = \left[0 + 0.5(0) - (-237{,}180)\right] + (900) - 0.5(3{,}970)$$

$$\bar{e}^{ch}_{H_2} = 236{,}100 \text{ kJ/kmol}$$

- ► This value for the chemical exergy of **H_2** agrees with the standard chemical exergy **(Model II)** from Table A-26, as expected.



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Octane	$C_8H_{18}(l)$	–	5,413,100
Ethanol	$C_2H_5OH(l)$	1,342,085	1,357,700

Standard Chemical Exergy

- The chemical exergy of hydrocarbon fuels are approximated by their fuel heating values. This can be illustrated using heating value data from Table A-25 and chemical exergy values **(Model II)** from Table A-26 converted to a unit mass basis, all in units of kJ/kg.
- For instance, using the liquid octane data,
  - $\mathbf{e^{ch}/HHV = 47{,}390/47{,}900 = 0.99}$
  - $\mathbf{e^{ch}/LHV = 47{,}390/44{,}430 = 1.07}$

Substance	Model for	HHV	LHV	e^{ch}
Liquid octane	Gasoline	47,900	44,430	47,390
Liquid ethanol	Biofuel gasoline substitute[a]	29,670	26,800	29,470[b]
Gaseous methane	Natural gas	55,510	50,020	51,850

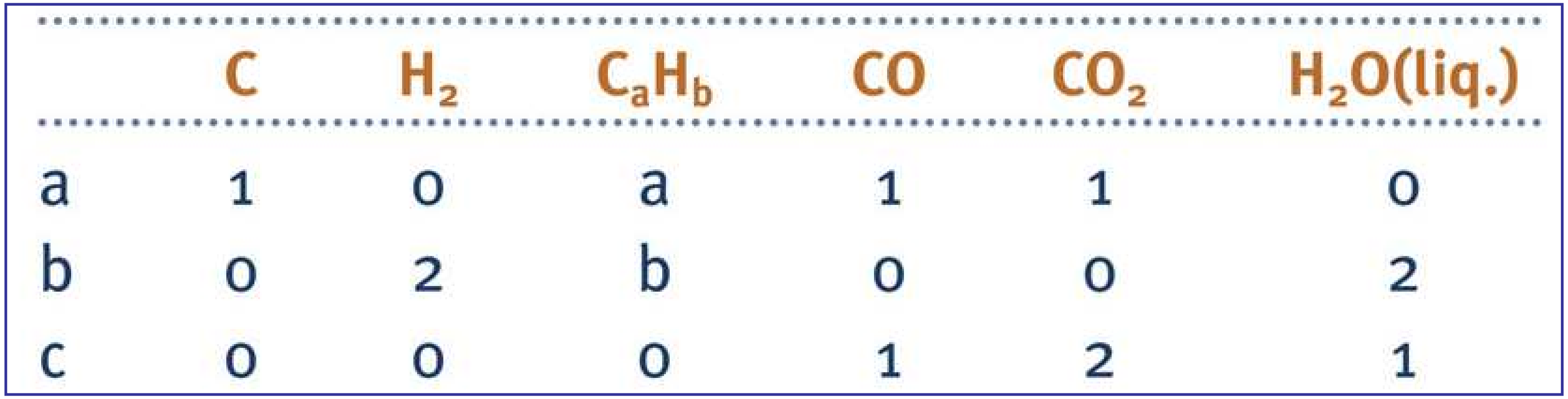
[a] In the U.S. today ethanol is made from the starch of corn kernels. In Brazil, which is also a major ethanol producer, sugar cane is used.

[b] On a mass basis, the chemical exergy of ethanol is about 2/3 of that for gasoline, thereby giving lower vehicle fuel mileage when using a blend such as E85 (85% ethanol, 15% gasoline).

Conceptualizing Chemical Exergy

►To reinforce understanding of the chemical exergy concept and the modeling used to develop working expressions for chemical exergy, let us consider a thought experiment involving:

1. A set of substances represented by $C_aH_bO_c$

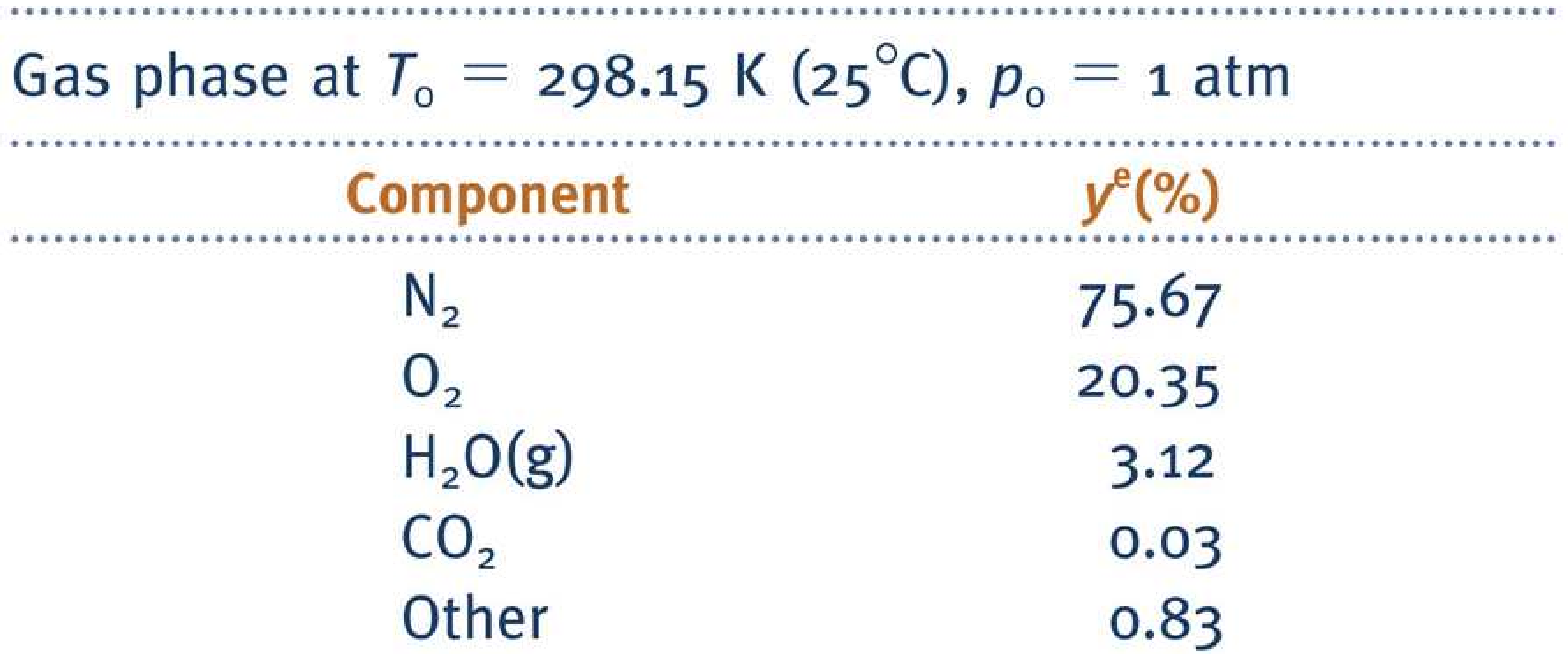


	C	H_2	C_aH_b	CO	CO_2	H_2O(liq.)
a	1	0	a	1	1	0
b	0	2	b	0	0	2
c	0	0	0	1	2	1

Conceptualizing Chemical Exergy

2. An exergy reference environment modeling Earth's atmosphere

Table 13.4. Exergy Reference Environment



Gas phase at $T_0 = 298.15$ K (25°C), $p_0 = 1$ atm

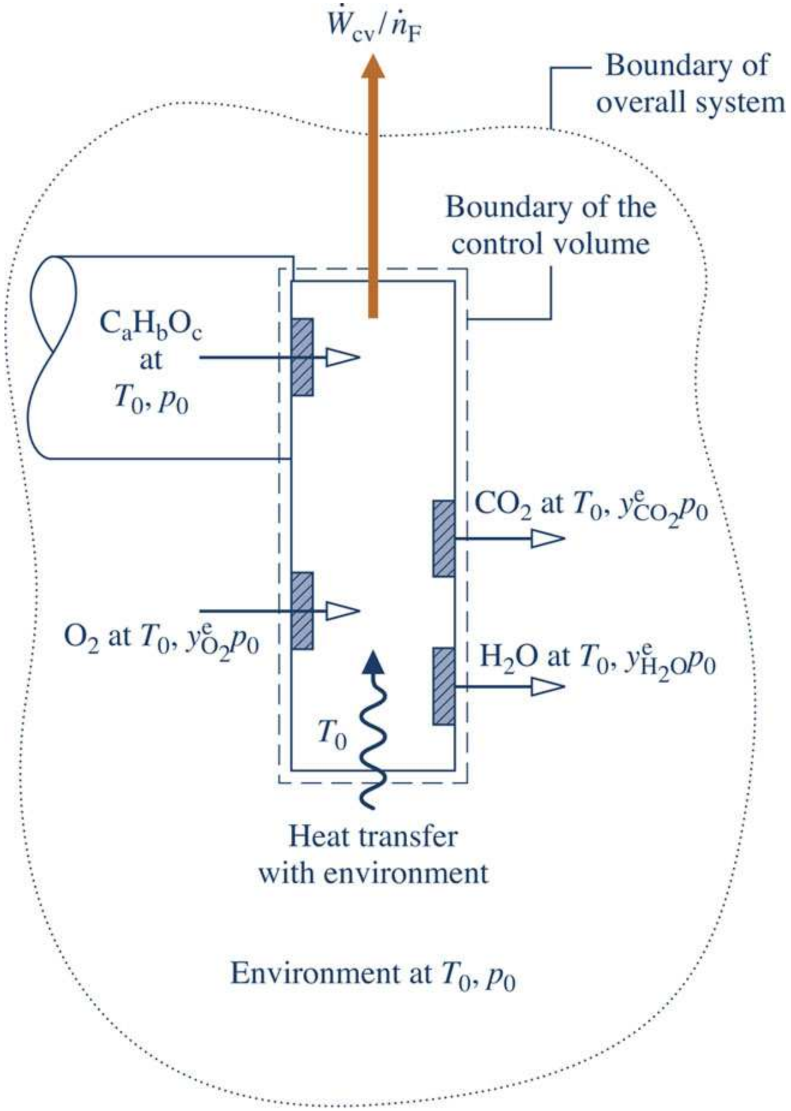
Component	$y^e(\%)$
N_2	75.67
O_2	20.35
$H_2O(g)$	3.12
CO_2	0.03
Other	0.83

►y^e denotes the mole fraction of an environmental component.

Conceptualizing Chemical Exergy

3. A system for visualizing how work can be obtained, in principle, from the difference in state of a substance represented as $\mathbf{C_aH_bO_c}$ at T_0, p_0 and an environment modeled as in the previous table.

   ►This is Fig. 13.6.

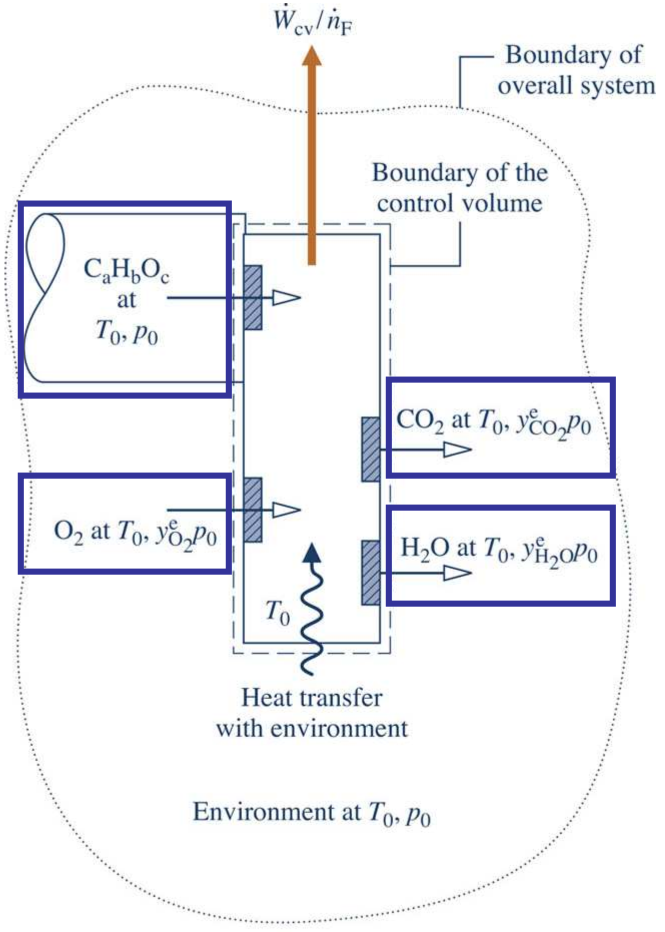


$$C_aH_bO_c + [a + b/4 - c/2]O_2 \rightarrow aCO_2 + b/2\ H_2O(g)$$

Conceptualizing Chemical Exergy

- Important aspects of Fig. 13.6 include

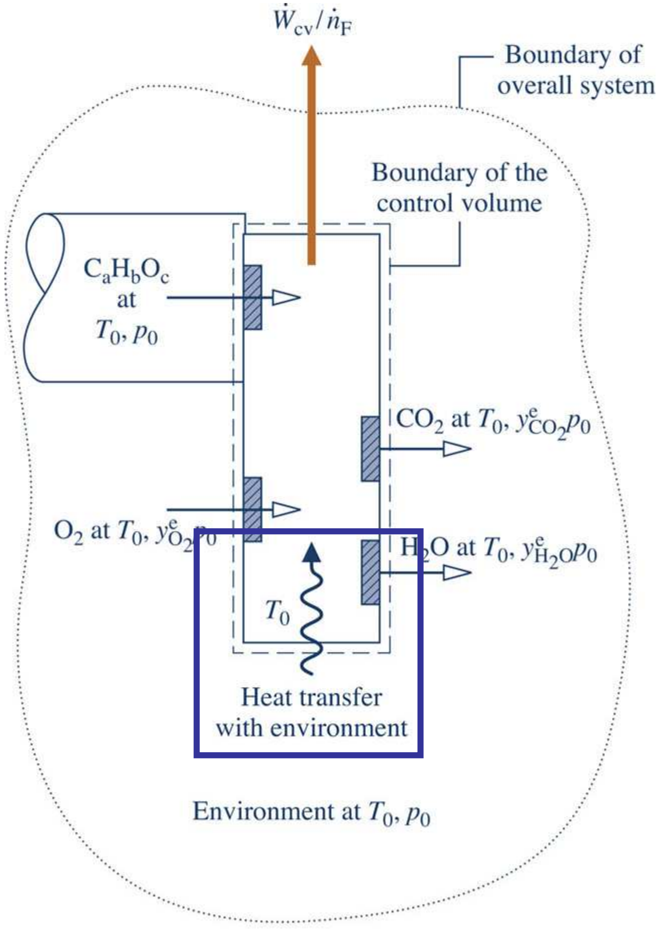
1. The substance represented as $\mathbf{C_aH_bO_c}$ enters the control volume at T_0, p_0.
2. Compounds present in the environment enter the control volume ($\mathbf{O_2}$) and exit the control volume ($\mathbf{CO_2}$, $\mathbf{H_2O(g)}$) at T_0 and their respective partial pressures.
3. The ideal gas model applies to $\mathbf{O_2}$, $\mathbf{CO_2}$, and $\mathbf{H_2O(g)}$.



$C_aH_bO_c + [a + b/4 - c/2]O_2 \rightarrow aCO_2 + b/2\ H_2O(g)$

Conceptualizing Chemical Exergy

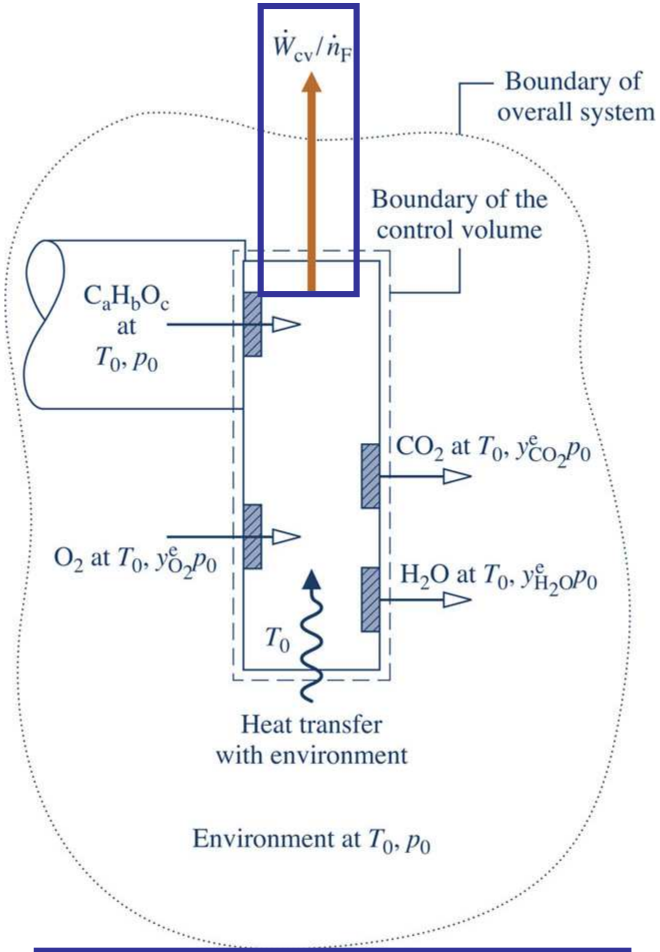
4. All substances enter and exit with negligible kinetic and potential energy effects.
5. Heat transfer between the control volume and environment occurs only at temperature T_0.
6. The control volume is at steady state.



$$C_aH_bO_c + [a + b/4 - c/2]O_2 \rightarrow aCO_2 + b/2\ H_2O(g)$$

Conceptualizing Chemical Exergy

7. For each substance represented as $\mathbf{C_aH_bO_c}$, the conservation of mass principle is embodied in the reaction equation provided in the figure, whether or not a reaction is required to conceive of the chemical exergy.
8. The chemical exergy per mole of $\mathbf{C_aH_bO_c}$, $\bar{\mathbf{e}}^{ch}$, is the maximum theoretical value of $\dot{W}_{cv}/\dot{n}_F$.



$$C_aH_bO_c + [a + b/4 - c/2]O_2 \rightarrow aCO_2 + b/2\ H_2O(g)$$

Conceptualizing Chemical Exergy

►Applying energy and entropy balances, and representing the result in terms of Gibbs functions for computational ease, we get

$$\bar{\mathrm{e}}^{\mathrm{ch}} = \boxed{\left[\bar{g}_{\mathrm{F}} + \left(\mathrm{a} + \frac{\mathrm{b}}{4} - \frac{\mathrm{c}}{2}\right)\bar{g}_{\mathrm{O_2}} - \mathrm{a}\bar{g}_{\mathrm{CO_2}} - \frac{\mathrm{b}}{2}\bar{g}_{\mathrm{H_2O(g)}}\right](T_0, p_0)}$$

$$+ \bar{R}T_0 \ln\left[\frac{(y^{\mathrm{e}}_{\mathrm{O_2}})^{\mathrm{a}+\mathrm{b}/4-\mathrm{c}/2}}{(y^{\mathrm{e}}_{\mathrm{CO_2}})^{\mathrm{a}}(y^{\mathrm{e}}_{\mathrm{H_2O}})^{\mathrm{b}/2}}\right] \quad \textbf{(Eq. 13.36)}$$

where the subscript **F** denotes the substance represented by $\mathbf{C_aH_bO_c}$.

►The coefficient of each of these Gibbs function terms corresponds to its coefficient in the reaction equation.

►The specific Gibbs functions are evaluated at the temperature T_0 and pressure p_0 of the environment.

►In the special case where T_0 = **298.15 K (25°C)** and p_0 = **1 atm**, the Gibbs function values can be simply read from Tables A-25, which provide data at **298.15 K, 1 atm**.

Conceptualizing Chemical Exergy

►Applying energy and entropy balances, and representing the result in terms of Gibbs functions for computational ease, we get

$$\bar{e}^{ch} = \left[\bar{g}_F + \left(a + \frac{b}{4} - \frac{c}{2}\right)\bar{g}_{O_2} - a\bar{g}_{CO_2} - \frac{b}{2}\bar{g}_{H_2O(g)}\right](T_0, p_0) + \boxed{\bar{R}T_0 \ln\left[\frac{(y^e_{O_2})^{a+b/4-c/2}}{(y^e_{CO_2})^{a}(y^e_{H_2O})^{b/2}}\right]}$$

(Eq. 13.36)

where the subscript **F** denotes the substance represented by $\mathbf{C_aH_bO_c}$.

- ►In the logarithmic term of **Eq. 13.36**, only the environmental substances $\mathbf{O_2}$, $\mathbf{CO_2}$, and $\mathbf{H_2O(g)}$ appear. Each exponent corresponds to the coefficient of that substance in the reaction equation.
- ►The logarithmic term typically contributes only a few percent to the chemical exergy magnitude.

Conceptualizing Chemical Exergy

Example: Consider the case of methane, CH_4, when T_0 = 298.15 K (25°C), p_0 = 1 atm.

- ►Refer to the reaction of Fig. 13.6:

$$C_aH_bO_c + [a + b/4 - c/2]O_2 \rightarrow aCO_2 + b/2\ H_2O(g)$$

- ►Here **a = 1, b = 4, c = 0** and the assumed reaction takes the form

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g)$$

- ►**Equation 13.36** reduces to

$$\overline{e}^{ch} = \overline{g}_F + 2\overline{g}_{O_2} - \overline{g}_{CO_2} - 2\overline{g}_{H_2O(g)} + \overline{R}T_0 \ln\left[\frac{\left(y^e_{O_2}\right)^2}{\left(y^e_{CO_2}\right)\left(y^e_{H_2O}\right)^2}\right] \qquad (1)$$

Conceptualizing Chemical Exergy

- For this application we can use Gibbs function data directly from Table A-25 since this source corresponds to **298.15 K, 1 atm**.

$$\bar{g}^{o}_{f,CH_4} = -50{,}790\ \text{kJ/kmol}$$

$$\bar{g}^{o}_{f,CO_2} = -394{,}380\ \text{kJ/kmol}$$

$$\bar{g}^{o}_{f,O_2} = 0\ \text{kJ/kmol}$$

$$\bar{g}^{o}_{f,H_2O(g)} = -228{,}590\ \text{kJ/kmol}$$

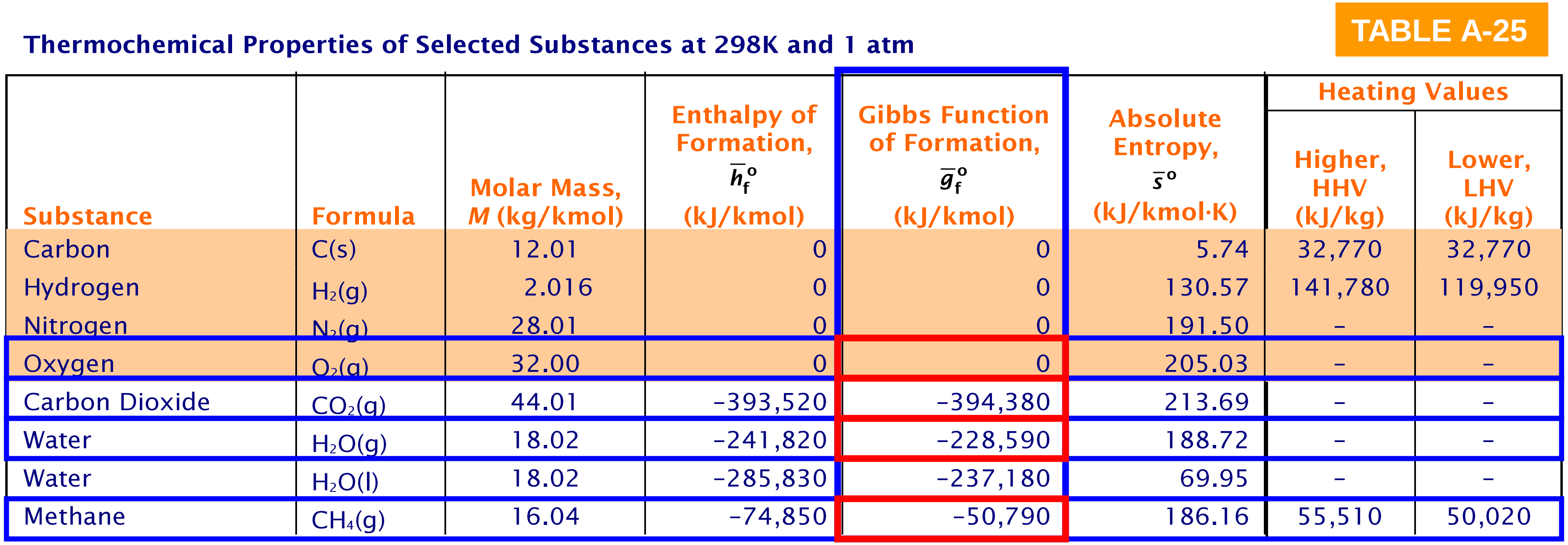


TABLE A-25

Thermochemical Properties of Selected Substances at 298K and 1 atm

Substance	Formula	Molar Mass, *M* (kg/kmol)	Enthalpy of Formation, $\bar{h}^{o}_{f}$ (kJ/kmol)	Gibbs Function of Formation, $\bar{g}^{o}_{f}$ (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 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	–	–
Methane	$CH_4(g)$	16.04	–74,850	–50,790	186.16	55,510	50,020

Conceptualizing Chemical Exergy

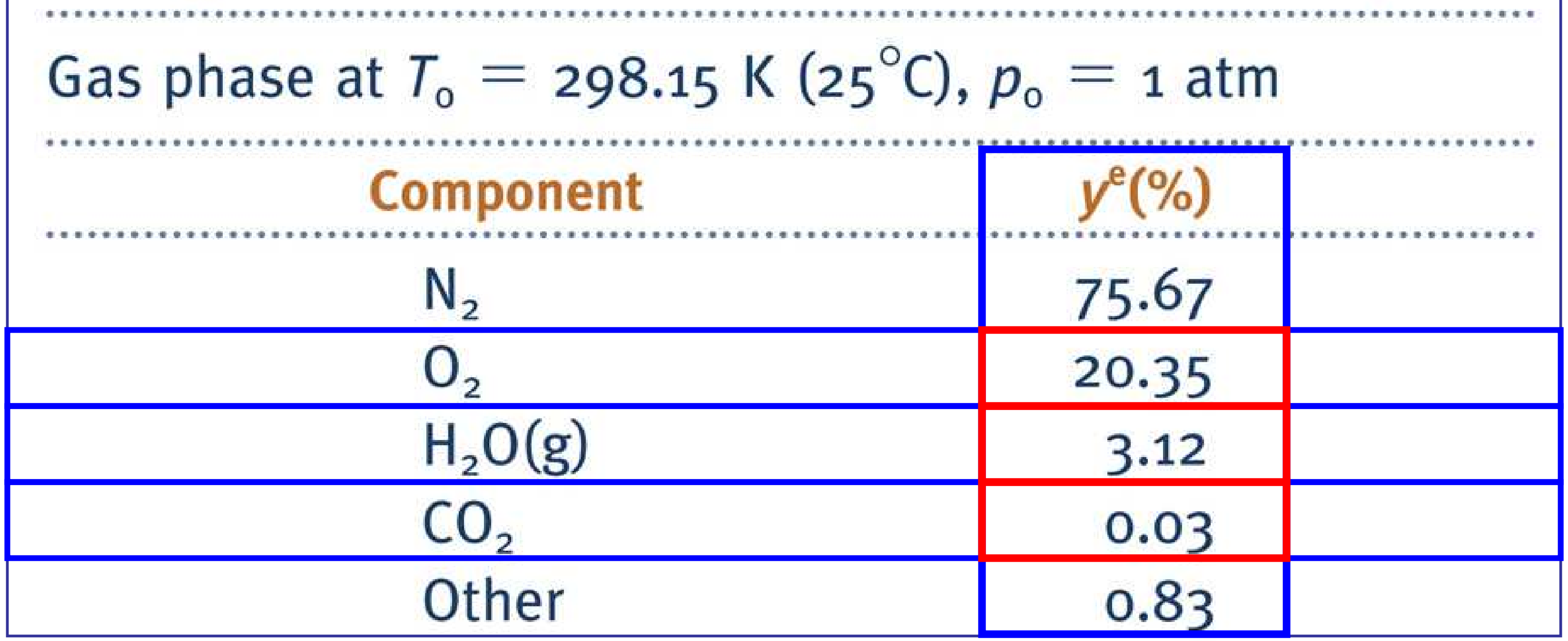
- From Table 13.4

$y^{e}_{O_2} = 0.2035$

$y^{e}_{CO_2} = 0.0003$

$y^{e}_{H_2O} = 0.0312$

Table 13.4. Exergy Reference Environment



Gas phase at T_o = 298.15 K (25°C), p_o = 1 atm

Component	y^e(%)
N_2	75.67
O_2	20.35
$H_2O(g)$	3.12
CO_2	0.03
Other	0.83

Conceptualizing Chemical Exergy

- Substituting values into **Eq. (1)**

$$\bar{e}^{ch} = \bar{g}_F + 2\bar{g}_{O_2} - \bar{g}_{CO_2} - 2\bar{g}_{H_2O(g)} + \bar{R}T_0 \ln\left[\frac{\left(y^e_{O_2}\right)^2}{\left(y^e_{CO_2}\right)\left(y^e_{H_2O}\right)^2}\right]$$

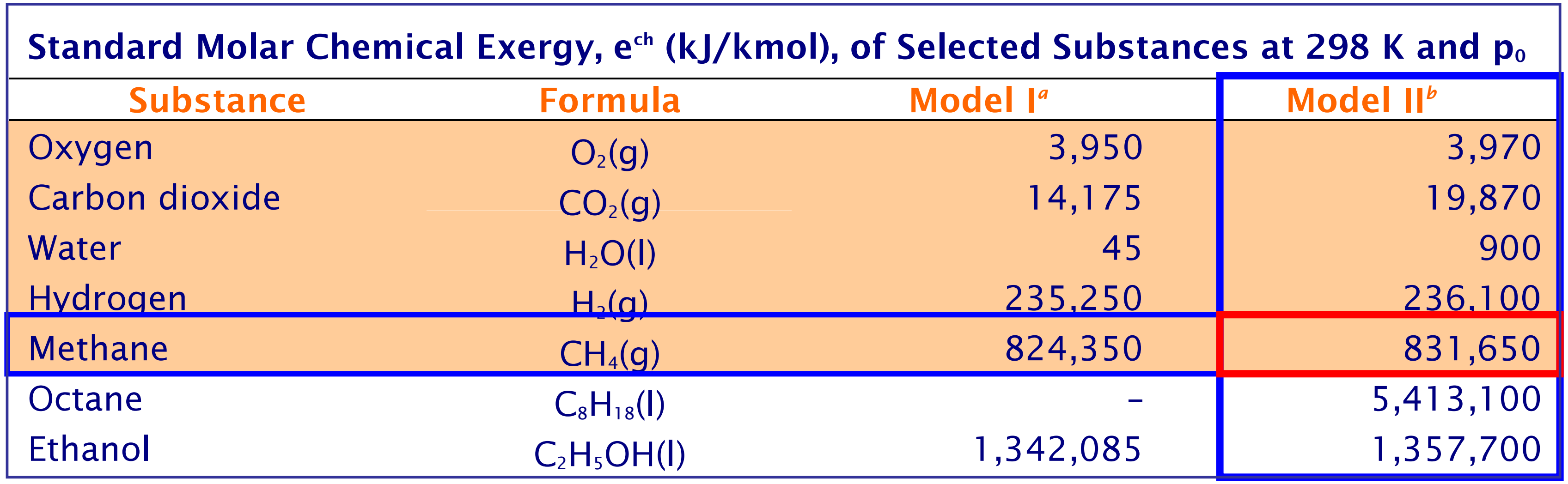
$$\bar{e}^{ch} = \left[-50{,}790 + 2(0) - (-394{,}380) - 2(-228{,}590)\right]\frac{\text{kJ}}{\text{kmol}}$$
$$+\left(8.314\frac{\text{kJ}}{\text{kmol}\cdot\text{K}}\right)(298.15\ \text{K})\ln\left[\frac{(0.2035)^2}{(0.0003)(0.0312)^2}\right]$$

$$\bar{e}^{ch} = 800{,}770\frac{\text{kJ}}{\text{kmol}} + 29{,}404\frac{\text{kJ}}{\text{kmol}}$$

$$\bar{e}^{ch} = 830{,}174\frac{\text{kJ}}{\text{kmol}}$$

Conceptualizing Chemical Exergy

- This value **(830,174 kJ/kmol)** for the chemical exergy of methane agrees with the standard chemical exergy **(Model II)** from Table A-26, which is **831,650 kJ/kmol**.



Standard Molar Chemical Exergy, e^{ch} (kJ/kmol), of Selected Substances at 298 K and p_0

Substance	Formula	Model I[a]	Model II[b]
Oxygen	$O_2(g)$	3,950	3,970
Carbon dioxide	$CO_2(g)$	14,175	19,870
Water	$H_2O(l)$	45	900
Hydrogen	$H_2(g)$	235,250	236,100
Methane	$CH_4(g)$	824,350	831,650
Octane	$C_8H_{18}(l)$	–	5,413,100
Ethanol	$C_2H_5OH(l)$	1,342,085	1,357,700

- This illustrates that the relatively elementary modeling of the environment used in developing **Eq.13.36** can yield chemical exergy values in harmony with published ***standard chemical exergy*** data.

Conceptualizing Chemical Exergy

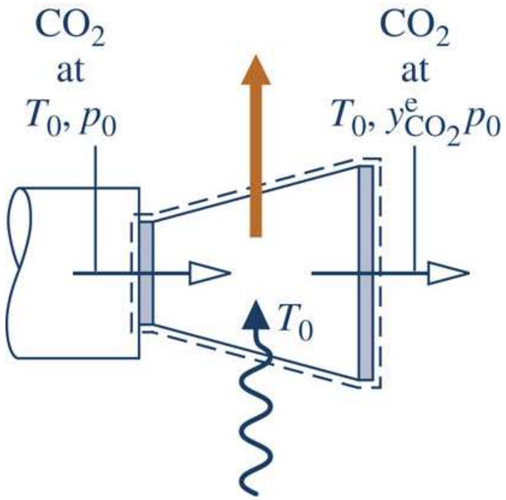
Example: Consider the case of carbon dioxide, $\mathbf{CO_2}$, when T_0 = **298.15 K (25°C)**, p_0 = **1 atm**.

►Here **a = 1, b = 0, c = 2** and the assumed reaction

$$\mathbf{C_aH_bO_c + [a + b/4 - c/2]O_2 \rightarrow aCO_2 + b/2\ H_2O(g)}$$

takes the form $\mathbf{CO_2 \rightarrow CO_2}$.

►In this case, $\mathbf{CO_2}$ enters the control volume of Fig. 13.6 at T_0, p_0 and exits at T_0 and the partial pressure $y^{e}_{CO_2}(p_0)$. No chemical reaction occurs.



►Rather, in this case we can think of the work that could be developed if the $\mathbf{CO_2}$ expands through a turbine from pressure p_0 to pressure $y^{e}_{CO_2}(p_0)$.

Conceptualizing Chemical Exergy

- ▶ With **a = 1, b = 0, c = 2**, **Eq. 13.36** reduces to

$$\bar{e}^{ch} = \bar{R}T_0 \ln\left[\frac{1}{(y^{e}_{CO_2})}\right]$$

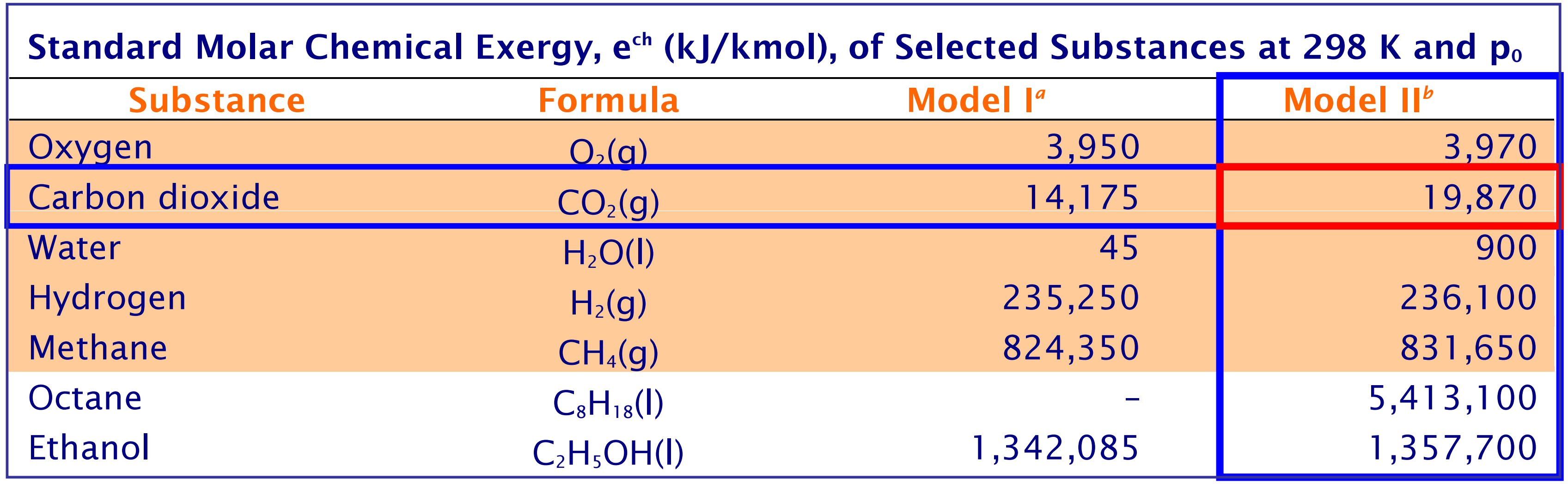
- ▶ With $y^{e}_{CO_2} = 0.0003$ from Table 13.4

$$\bar{e}^{ch} = \left(8.314\frac{\text{kJ}}{\text{kmol}\cdot\text{K}}\right)(298.15\,\text{K})\ln\left[\frac{1}{(0.0003)}\right]$$

$$\bar{e}^{ch} = 20{,}108\frac{\text{kJ}}{\text{kmol}}$$

Conceptualizing Chemical Exergy

- This value **(20,108 kJ/kmol)** for the chemical exergy of carbon dioxide agrees with the standard chemical exergy **(Model II)** from Table A-26, which is **19,870 kJ/kmol**.



Standard Molar Chemical Exergy, e^{ch} (kJ/kmol), of Selected Substances at 298 K and p_0

Substance	Formula	Model I[a]	Model II[b]
Oxygen	$O_2(g)$	3,950	3,970
Carbon dioxide	$CO_2(g)$	14,175	19,870
Water	$H_2O(l)$	45	900
Hydrogen	$H_2(g)$	235,250	236,100
Methane	$CH_4(g)$	824,350	831,650
Octane	$C_8H_{18}(l)$	–	5,413,100
Ethanol	$C_2H_5OH(l)$	1,342,085	1,357,700

- This illustrates that the relatively elementary modeling of the environment used in developing **Eq.13.36** can yield chemical exergy values in harmony with published ***standard chemical exergy*** data.