A mixture of $H_2$ and $O_2$ in a tank is ignited. The equilibrium composition of the product gases and the amount of heat transfer from the combustion chamber are to be determined.

**Assumptions**

1. The equilibrium composition consists of $H_2O$, $H_2$, and $O_2$.
2. The constituents of the mixture are ideal gases.

**Analysis**

(a) The combustion equation can be written as

$$H_2 + 0.5O_2 \longrightarrow xH_2O + (1-x)H_2 + (0.5-0.5x)O_2$$

The equilibrium equation among $H_2O$, $H_2$, and $O_2$ can be expressed as

$$H_2O \Leftrightarrow H_2 + \frac{1}{2}O_2 \quad (\text{thus } v_{H_2} = 1, \quad v_{H_2} = 1, \quad v_{O_2} = \frac{1}{2})$$

Total number of moles: $N_{\text{total}} = x + (1-x) + (0.5-0.5x) = 1.5-0.5x$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{H_2}^{v_{H_2}}N_{O_2}^{v_{O_2}}}{N_{H_2O}^{v_{H_2O}}} \left( \frac{P}{N_{\text{total}}} \right)^{(v_{H_2} + v_{O_2} - v_{H_2O})}$$

From Table A-28, $\ln K_p = -3.812$ at 2800 K. Thus $K_p = 0.02210$. Substituting,

$$0.0221 = \frac{(1-x)(0.5-0.5x)^{0.5}}{x} \left( \frac{5}{1.5-0.5x} \right)^{1+0.5-1}$$

Solving for $x$, $x = 0.944$

Then the combustion equation and the equilibrium composition can be expressed as

$$H_2 + 0.5O_2 \longrightarrow 0.944H_2O + 0.056H_2 + 0.028O_2$$

and

$$0.944H_2O + 0.056H_2 + 0.028O_2$$

(b) The heat transfer can be determined from

$$-Q_{\text{out}} = \sum N_R \left( \bar{h}_f^T + \bar{h} - \bar{h}^* - P\bar{\sigma} \right)_R - \sum N_R \left( \bar{h}_f^* + \bar{h} - \bar{h}^* - P\bar{\sigma} \right)_R$$

Since $W = 0$ and both the reactants and the products are assumed to be ideal gases, all the internal energy and enthalpies depend on temperature only, and the $P\bar{\sigma}$ terms in this equation can be replaced by $R_uT$. It yields

$$-Q_{\text{out}} = \sum N_R \left( \bar{h}_f^T + \bar{h}_{298\text{K}} - \bar{h}_{298\text{K}} - R_uT \right)_R - \sum N_R \left( \bar{h}_f^* - R_uT \right)_R$$

since reactants are at the standard reference temperature of 25°C. From the tables,

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\bar{h}_f^T$ kJ/kmol</th>
<th>$\bar{h}_{298\text{K}}$ kJ/kmol</th>
<th>$\bar{h}_{2800\text{K}}$ kJ/kmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>0</td>
<td>8468</td>
<td>89,838</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0</td>
<td>8682</td>
<td>98,826</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>-241,820</td>
<td>9904</td>
<td>125,198</td>
</tr>
</tbody>
</table>

Substituting,

$$-Q_{\text{out}} = 0.944(-241,820 + 125,198 - 9904 - 8.314 \times 2800) + 0.056(0 + 89,838 - 8468 - 8.314 \times 2800) + 0.028(0 + 98,826 - 8682 - 8.314 \times 2800) - 1(0 - 8.314 \times 298) - 0.5(0 - 8.314 \times 298)$$

$$= -132,574 \text{ kJ/kmol H}_2$$

or

$$Q_{\text{out}} = 132,574 \text{ kJ/mol H}_2$$

The equilibrium constant for the reaction $H_2O \Leftrightarrow OH + \frac{1}{2}H_2$ is $\ln K_p = -3.763$, which is very close to the $K_p$ value of the reaction considered. Therefore, it is not realistic to assume that no OH will be present in equilibrium mixture.
A mixture of H$_2$O and O$_2$ is heated to a high temperature. The equilibrium composition is to be determined.

**Assumptions** 1 The equilibrium composition consists of H$_2$O, OH, O$_2$, and H$_2$. 2 The constituents of the mixture are ideal gases.

**Analysis** The reaction equation during this process can be expressed as

\[2\text{H}_2\text{O} + 3\text{O}_2 \rightarrow x\text{H}_2\text{O} + y\text{H}_2 + z\text{O}_2 + w\text{OH}\]

Mass balances for hydrogen and oxygen yield

H balance: \[4 = 2x + 2y + w\] (1)

O balance: \[8 = x + 2z + w\] (2)

The mass balances provide us with only two equations with four unknowns, and thus we need to have two more equations (to be obtained from the $K_P$ relations) to determine the equilibrium composition of the mixture. They are

\[\text{H}_2\text{O} \rightleftharpoons \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{O}_2\] (reaction 1)

\[\text{H}_2\text{O} \rightleftharpoons \frac{1}{2}\text{H}_2 + \text{OH}\] (reaction 2)

The equilibrium constant for these two reactions at 3600 K are determined from Table A-28 to be

\[
\ln K_{p1} = -1.392 \quad \rightarrow \quad K_{p1} = 0.24858
\]

\[
\ln K_{p2} = -1.088 \quad \rightarrow \quad K_{p2} = 0.33689
\]

The $K_P$ relations for these two simultaneous reactions are

\[
K_{p1} = \frac{N_{\text{H}_2}^{y_{\text{H}_2}} \cdot N_{\text{O}_2}^{y_{\text{O}_2}} \cdot P^{y_{\text{H}_2} + y_{\text{O}_2} - y_{\text{H}_2}\text{O}_2}}{N_{\text{H}_2\text{O}}^{x_{\text{H}_2\text{O}}}}
\]

\[
K_{p2} = \frac{N_{\text{H}_2}^{y_{\text{H}_2}} \cdot N_{\text{OH}}^{y_{\text{OH}}}}{N_{\text{H}_2\text{O}}^{x_{\text{H}_2\text{O}}}} \cdot \frac{P^{y_{\text{H}_2} + y_{\text{OH}} - y_{\text{H}_2}\text{OH}}}{N_{\text{H}_2\text{O}}^{x_{\text{H}_2\text{O}}}}
\]

where

\[N_{\text{H}_2\text{O}} = N_{\text{H}_2}\text{O} + N_{\text{H}_2} + N_{\text{O}_2} + N_{\text{OH}} = x + y + z + w\]

Substituting,

\[
0.24858 = \frac{(y)(z)^{1/2}}{x} \left( \frac{8}{x + y + z + w} \right)^{1/2}
\] (3)

\[
0.33689 = \frac{(w)(y)^{1/2}}{x} \left( \frac{8}{x + y + z + w} \right)^{1/2}
\] (4)

Solving Eqs. (1), (2), (3), and (4) simultaneously for the four unknowns $x$, $y$, $z$, and $w$ yields

\[x = 1.371, \quad y = 0.1646, \quad z = 2.85, \quad w = 0.928\]

Therefore, the equilibrium composition becomes

\[1.371\text{H}_2\text{O} + 0.165\text{H}_2 + 2.85\text{O}_2 + 0.928\text{OH}\]
A mixture of CO\(_2\) and O\(_2\) is heated to a high temperature. The equilibrium composition is to be determined.

**Assumptions**
1. The equilibrium composition consists of CO\(_2\), CO, O\(_2\), and O.
2. The constituents of the mixture are ideal gases.

**Analysis**
The reaction equation during this process can be expressed as

\[
3\text{C}_2\text{O} + 3\text{O}_2 \rightleftharpoons x\text{CO}_2 + y\text{CO} + z\text{O}_2 + w\text{O}
\]

Mass balances for carbon and oxygen yield

C balance: \(3 = x + y\) \hspace{1cm} (1)

O balance: \(12 = 2x + 2y + 2z + w\) \hspace{1cm} (2)

The mass balances provide us with only two equations with four unknowns, and thus we need to have two more equations (to be obtained from the \(K_P\) relations) to determine the equilibrium composition of the mixture. They are

\[
\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2 \quad \text{(reaction 1)}
\]

\[
\text{O}_2 \rightleftharpoons 2\text{O} \quad \text{(reaction 2)}
\]

The equilibrium constant for these two reactions at 3400 K are determined from Table A-28 to be

\[
\ln K_{P1} = 0.169 \quad \rightarrow \quad K_{P1} = 1.1841
\]

\[
\ln K_{P2} = -1.935 \quad \rightarrow \quad K_{P2} = 0.1444
\]

The \(K_P\) relations for these two simultaneous reactions are

\[
K_{P1} = \frac{N_{\text{CO}}^{y_{\text{CO}_2}} N_{\text{O}_2}^{y_{\text{O}_2}}}{N_{\text{CO}_2}^{y_{\text{CO}_2}}} \left( \frac{P}{N_{\text{total}}} \right)^{y_{\text{CO}_2} + y_{\text{O}_2} - y_{\text{CO}_2}}
\]

\[
K_{P2} = \frac{N_{\text{O}}^{y_{\text{O}_2}}}{N_{\text{O}_2}^{y_{\text{O}_2}}} \left( \frac{P}{N_{\text{total}}} \right)^{y_{\text{O}_2} - y_{\text{O}_2}}
\]

where

\[
N_{\text{total}} = N_{\text{CO}_2} + N_{\text{O}_2} + N_{\text{CO}} + N_{\text{O}} = x + y + z + w
\]

Substituting,

\[
1.1841 = \left( \frac{y(z)}{x} \right)^{1/2} \left( \frac{2}{x + y + z + w} \right)^{1/2} \hspace{1cm} (3)
\]

\[
0.1444 = \frac{w^2}{z} \left( \frac{2}{x + y + z + w} \right)^{2-1} \hspace{1cm} (4)
\]

Solving Eqs. (1), (2), (3), and (4) simultaneously for the four unknowns \(x, y, z,\) and \(w\) yields

\[
x = 1.313 \quad y = 1.687 \quad z = 3.187 \quad w = 1.314
\]

Thus the equilibrium composition is

\[
1.313\text{CO}_2 + 1.687\text{CO} + 3.187\text{O}_2 + 1.314\text{O}
\]
**16-86 EES** Problem 16-85 is reconsidered. The effect of pressure on the equilibrium composition by varying pressure from 1 atm to 10 atm is to be studied.

**Analysis** The problem is solved using EES, and the solution is given below.

"For EES to calculate a, b, c, and d at T_prod and P_prod press F2 or click on the Calculator icon. The EES results using the built in function data is not the same as the answers provided with the problem. However, if we supply the K_P's from Table A-28 to ESS, the results are equal to the answer provided. The plot of moles CO vs. P_atm was done with the EES property data."

"Input Data"
P_atm = 2 [atm]
P_prod =P_atm*101.3
R_u=8.314 [kJ/kmol-K]
T_prod=3400 [K]
P=P_atm

"For the incomplete combustion process in this problem, the combustion equation is
3 CO2 + 3 O2=aCO2 +bCO + cO2+dO"

"Specie balance equations"
"O"
3*2+3*2=a +2+b +c +2+d*1
"C"
3*1=a +b*1
N_tot =a +b +c +d "Total kilomoles of products at equilibrium"

"We assume the equilibrium reactions are
CO2=CO+0.5O2
O2=2O"

"The following equations provide the specific Gibbs function (g=h-Ts) for each component as a function of its temperature at 1 atm pressure, 101.3 kPa"
g_CO2=Enthalpy(CO2,T=T_prod)-T_prod *Entropy(CO2,T=T_prod,P=101.3)
g_CO=Enthalpy(CO,T=T_prod)-T_prod *Entropy(CO,T=T_prod,P=101.3)
g_O2=Enthalpy(O2,T=T_prod)-T_prod *Entropy(O2,T=T_prod,P=101.3)

"EES does not have a built-in property function for monatomic oxygen so we will use the JANAF procedure, found under Options/Function Info/External Procedures. The units for the JANAF procedure are kmol, K, and kJ. The values are calculated for 1 atm. The entropy must be corrected for other pressurues."

Call JANAF('O',T Prod:Cp,p,O,s_O) "Units from JANAF are SI"
"The entropy from JANAF is for one atmosphere and that's what we need for this approach."
g_O=h_O-T_prod*s_O

"The standard-state (at 1 atm) Gibbs functions are"
DELTAG_1 =1* g_CO+0.5* g_O2-1* g_CO2
DELTAG_2 =2* g_O-1* g_O2

"The equilibrium constants are given by Eq. 15-14."
\[ K_P_2=0.1444 \] From Table A-28
\[ K_P_1 = 0.8445 \] From Table A-28
\[ K_p_1 = \exp(-DELTAG_1/(R_u*T_prod)) \] From EES data
\[ K_P_2 = \exp(-DELTAG_2/(R_u*T_prod)) \] From EES data

"The equilibrium constant is also given by Eq. 15-15."
"Write the equilibrium constant for the following system of equations:
3 CO2 + 3 O2 = aCO2 + bCO + cO2 + dO
CO2 = CO + 0.5O2
O2 = 2O"

"K_P_1 = (P/N_tot)^(1+0.5-1)*(b^1*c^0.5)/(a^1)"
sqrt(P/N_tot )*b *sqrt(c )/a=K_P_1

"K_P_2 = (P/N_tot)^(2-1)*(d^2)/(c^1)"
P/N_tot *d^2/c =K_P_2

<table>
<thead>
<tr>
<th>b [kmol CO]</th>
<th>P_atm [atm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.968</td>
<td>1</td>
</tr>
<tr>
<td>1.687</td>
<td>2</td>
</tr>
<tr>
<td>1.52</td>
<td>3</td>
</tr>
<tr>
<td>1.404</td>
<td>4</td>
</tr>
<tr>
<td>1.315</td>
<td>5</td>
</tr>
<tr>
<td>1.244</td>
<td>6</td>
</tr>
<tr>
<td>1.186</td>
<td>7</td>
</tr>
<tr>
<td>1.136</td>
<td>8</td>
</tr>
<tr>
<td>1.093</td>
<td>9</td>
</tr>
<tr>
<td>1.055</td>
<td>10</td>
</tr>
</tbody>
</table>

PROPRIETARY MATERIAL. © 2006 The McGraw-Hill Companies, Inc. Limited distribution permitted only to teachers and educators for course preparation. If you are a student using this Manual, you are using it without permission.
The $\overline{h}_R$ at a specified temperature is to be determined using enthalpy and $K_p$ data.

**Assumptions** Both the reactants and products are ideal gases.

**Analysis**

(a) The complete combustion equation of $\text{H}_2$ can be expressed as

$$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$$

The $\overline{h}_R$ of the combustion process of $\text{H}_2$ at 2400 K is the amount of energy released as one kmol of $\text{H}_2$ is burned in a steady-flow combustion chamber at a temperature of 2400 K, and can be determined from

$$\overline{h}_R = \sum N_P (\overline{h}_f^p + \overline{h} - \overline{h}^*)_P - \sum N_R (\overline{h}_f^r + \overline{h} - \overline{h}^*)_R$$

Assuming the $\text{H}_2\text{O}$, $\text{H}_2$, and $\text{O}_2$ to be ideal gases, we have $h = h(T)$. From the tables,

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\overline{h}_f^{\text{v}}$</th>
<th>$\overline{h}_{298 \text{K}}$</th>
<th>$\overline{h}_{2400 \text{K}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>-241,820</td>
<td>9904</td>
<td>103,508</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>0</td>
<td>8468</td>
<td>75,383</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>0</td>
<td>8682</td>
<td>83,174</td>
</tr>
</tbody>
</table>

Substituting,

$$\overline{h}_R = 1(-241,820 + 103,508 - 9904)$$

$$-1(0 + 75,383 - 8468)$$

$$-0.5(0 + 83,174 - 8682)$$

$$= -252,377 \text{ kJ/ kmol}$$

(b) The $\overline{h}_R$ value at 2400 K can be estimated by using $K_p$ values at 2200 K and 2600 K (the closest two temperatures to 2400 K for which $K_p$ data are available) from Table A-28,

$$\ln \frac{K_{p2}}{K_{p1}} \equiv \frac{\overline{h}_R}{R_u} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

or

$$\ln K_{p2} - \ln K_{p1} \equiv \frac{\overline{h}_R}{R_u} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$4.648 - 6.768 = \frac{\overline{h}_R}{8.314 \text{ kJ/kmol} \cdot \text{K}} \left( \frac{1}{2200 \text{ K}} - \frac{1}{2600 \text{ K}} \right)$$

$$\overline{h}_R \equiv -252,047 \text{ kJ/kmol}$$
16-88 EES  Problem 16-87 is reconsidered. The effect of temperature on the enthalpy of reaction using both methods by varying the temperature from 2000 to 3000 K is to be investigated.

**Analysis**  The problem is solved using EES, and the solution is given below.

"Input Data"

\[ T_{\text{prod}} = 2400 \text{ [K]} \]
\[ \Delta T_{\text{prod}} = 25 \text{ [K]} \]
\[ R_u = 8.314 \text{ [kJ/kmol-K]} \]
\[ T_{\text{prod}1} = T_{\text{prod}} - \Delta T_{\text{prod}} \]
\[ T_{\text{prod}2} = T_{\text{prod}} + \Delta T_{\text{prod}} \]

"The combustion equation is

\[ 1 \text{ H}_2 + 0.5 \text{ O}_2 \Rightarrow 1 \text{ H}_2\text{O} \]

"The enthalpy of reaction \( H_{\text{bar R}} \) using enthalpy data is:

\[ H_{\text{bar R}} = H_P - H_R \]

\[ H_P = 1*\text{Enthalpy(H}_2\text{O,T=T}_{\text{prod}}) \]
\[ H_R = 1*\text{Enthalpy(H}_2\text{,T=T}_{\text{prod}}) + 0.5*\text{Enthalpy(O}_2\text{,T=T}_{\text{prod}}) \]

"The enthalpy of reaction \( H_{\text{bar R}} \) using enthalpy data is found using the following equilibrium data:

"The following equations provide the specific Gibbs function (g=h-Ts) for each component as a function of its temperature at 1 atm pressure, 101.3 kPa"

\[ g_{\text{H}_2\text{O}1} = \text{Enthalpy(H}_2\text{O,T=T}_{\text{prod}1}) - T_{\text{prod}1}*\text{Entropy(H}_2\text{O,T=T}_{\text{prod}1},P=101.3) \]
\[ g_{\text{H}_21} = \text{Enthalpy(H}_2\text{,T=T}_{\text{prod}1}) - T_{\text{prod}1}*\text{Entropy(H}_2\text{,T=T}_{\text{prod}1},P=101.3) \]
\[ g_{\text{O}_21} = \text{Enthalpy(O}_2\text{,T=T}_{\text{prod}1}) - T_{\text{prod}1}*\text{Entropy(O}_2\text{,T=T}_{\text{prod}1},P=101.3) \]
\[ g_{\text{H}_2\text{O}2} = \text{Enthalpy(H}_2\text{O,T=T}_{\text{prod}2}) - T_{\text{prod}2}*\text{Entropy(H}_2\text{O,T=T}_{\text{prod}2},P=101.3) \]
\[ g_{\text{H}_22} = \text{Enthalpy(H}_2\text{,T=T}_{\text{prod}2}) - T_{\text{prod}2}*\text{Entropy(H}_2\text{,T=T}_{\text{prod}2},P=101.3) \]
\[ g_{\text{O}_22} = \text{Enthalpy(O}_2\text{,T=T}_{\text{prod}2}) - T_{\text{prod}2}*\text{Entropy(O}_2\text{,T=T}_{\text{prod}2},P=101.3) \]

"The standard-state (at 1 atm) Gibbs functions are"

\[ \Delta G_1 = 1* g_{\text{H}_2\text{O}1} - 0.5* g_{\text{O}_21} - 1* g_{\text{H}_21} \]
\[ \Delta G_2 = 1* g_{\text{H}_2\text{O}2} - 0.5* g_{\text{O}_22} - 1* g_{\text{H}_22} \]

"The equilibrium constants are given by Eq. 15-14."

\[ K_p_{1} = \exp(-\Delta G_1/(R_u*T_{\text{prod}1})) \] "From EES data"
\[ K_p_{2} = \exp(-\Delta G_2/(R_u*T_{\text{prod}2})) \] "From EES data"

"The enthalpy of reaction is estimated from the equilibrium constant \( K_p \) by using EQ 15-18 as:

\[ \ln(K_p/1) = h_{\text{bar R,enthalpy}} - R_u*(1/T_{\text{prod}1} - 1/T_{\text{prod}2}) \]

\[ \text{PercentError} = \text{ABS}(h_{\text{bar R,enthalpy}} - h_{\text{bar R,Kp}})*\text{Convert(, %)} \]

<table>
<thead>
<tr>
<th>Percent Error [%]</th>
<th>T_{\text{prod}1} [K]</th>
<th>H_{\text{R,enthalpy}} [kJ/kmol]</th>
<th>H_{\text{R,Kp}} [kJ/kmol]</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>0.00003095</td>
<td>3000</td>
<td>-253250</td>
<td>-253250</td>
</tr>
</tbody>
</table>

**DELTAT_{prod} = 25 K**

- Enthalpy Data
- Kp Data
The $K_P$ value of the dissociation process $\text{O}_2 \leftrightarrow 2\text{O}$ at a specified temperature is to be determined using the $\overline{h}_R$ data and $K_P$ value at a specified temperature.

**Assumptions** Both the reactants and products are ideal gases.

**Analysis** The $\overline{h}_R$ and $K_P$ data are related to each other by

$$\ln \frac{K_{P2}}{K_{P1}} \equiv \frac{\overline{h}_R}{R_u} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{or} \quad \ln K_{P2} - \ln K_{P1} \equiv \frac{\overline{h}_R}{R_u} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

The $\overline{h}_R$ of the specified reaction at 2800 K is the amount of energy released as one kmol of $\text{O}_2$ dissociates in a steady-flow combustion chamber at a temperature of 2800 K, and can be determined from

$$\overline{h}_R = \sum N_p \left( \overline{h}_f^{+} + \overline{h}^{-} \right)_p - \sum N_R \left( \overline{h}_f^{+} + \overline{h}^{-} \right)_R$$

Assuming the $\text{O}_2$ and $\text{O}$ to be ideal gases, we have $h = h(T)$. From the tables,

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\overline{h}_f^{n}$</th>
<th>$\overline{h}_{298\text{K}}$</th>
<th>$\overline{h}_{2800\text{K}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}$</td>
<td>249,190</td>
<td>6852</td>
<td>59,241</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>0</td>
<td>8682</td>
<td>98,826</td>
</tr>
</tbody>
</table>

Substituting,

$$\overline{h}_R = 2(249,190 + 59,241 - 6852) - 1(0 + 98,826 - 8682) = 513,014 \text{ kJ/kmol}$$

The $K_P$ value at 3000 K can be estimated from the equation above by using this $\overline{h}_R$ value and the $K_P$ value at 2600 K which is $\ln K_{P1} = -7.521$,

$$\ln K_{P2} - (-7.521) = \frac{513,014 \text{ kJ/kmol}}{8.314 \text{ kJ/kmol} \cdot \text{K}} \left( \frac{1}{2600 \text{ K}} - \frac{1}{3000 \text{ K}} \right)$$

$$\ln K_{P2} = -4.357 \quad (\text{Table A-28: } \ln K_{P2} = -4.357)$$

or $K_{P2} = 0.0128$
16-90 It is to be shown that when the three phases of a pure substance are in equilibrium, the specific Gibbs function of each phase is the same.

**Analysis** The total Gibbs function of the three phase mixture of a pure substance can be expressed as

\[ G = m_s g_s + m_l g_l + m_g g_g \]

where the subscripts \( s \), \( l \), and \( g \) indicate solid, liquid and gaseous phases. Differentiating by holding the temperature and pressure (thus the Gibbs functions, \( g \)) constant yields

\[ dG = g_s dm_s + g_l dm_l + g_g dm_g \]

From conservation of mass,

\[ dm_s + dm_l + dm_g = 0 \quad \rightarrow \quad dm_s = -dm_l - dm_g \]

Substituting,

\[ dG = -g_s(dm_l + dm_g) + g_l dm_l + g_g dm_g \]

Rearranging,

\[ dG = (g_l - g_s)dm_l + (g_g - g_s)dm_g \]

For equilibrium, \( dG = 0 \). Also \( dm_l \) and \( dm_g \) can be varied independently. Thus each term on the right hand side must be zero to satisfy the equilibrium criteria. It yields

\[ g_l = g_s \quad \text{and} \quad g_g = g_s \]

Combining these two conditions gives the desired result,

\[ g_l = g_s = g_g \]

16-91 It is to be shown that when the two phases of a two-component system are in equilibrium, the specific Gibbs function of each phase of each component is the same.

**Analysis** The total Gibbs function of the two phase mixture can be expressed as

\[ G = (m_{l1} g_{l1} + m_{g1} g_{g1}) + (m_{l2} g_{l2} + m_{g2} g_{g2}) \]

where the subscripts \( l \) and \( g \) indicate liquid and gaseous phases. Differentiating by holding the temperature and pressure (thus the Gibbs functions) constant yields

\[ dG = g_{l1} dm_{l1} + g_{g1} dm_{g1} + g_{l2} dm_{l2} + g_{g2} dm_{g2} \]

From conservation of mass,

\[ dm_{g1} = -dm_{l1} \quad \text{and} \quad dm_{g2} = -dm_{l2} \]

Substituting,

\[ dG = (g_{l1} - g_{g1})dm_{l1} + (g_{l2} - g_{g2})dm_{l2} \]

For equilibrium, \( dG = 0 \). Also \( dm_{l1} \) and \( dm_{l2} \) can be varied independently. Thus each term on the right hand side must be zero to satisfy the equilibrium criteria. Then we have

\[ g_{l1} = g_{g1} \quad \text{and} \quad g_{l2} = g_{g2} \]

which is the desired result.
A mixture of CO and O\textsubscript{2} contained in a tank is ignited. The final pressure in the tank and the amount of heat transfer are to be determined.

**Assumptions**
1. The equilibrium composition consists of CO\textsubscript{2} and O\textsubscript{2}.
2. Both the reactants and the products are ideal gases.

**Analysis**
The combustion equation can be written as

\[ CO + 3O_2 \rightarrow CO_2 + 2.5O_2 \]

The heat transfer can be determined from

\[ -Q_{out} = \sum N_P (\bar{h}_f + \bar{h} - P\bar{\sigma})_P - \sum N_R (\bar{h}_f + \bar{h} - P\bar{\sigma})_R \]

Both the reactants and the products are assumed to be ideal gases, and thus all the internal energy and enthalpies depend on temperature only, and the \( P\bar{\sigma} \) terms in this equation can be replaced by \( R_u T \). It yields

\[ -Q_{out} = \sum N_P (\bar{h}_f + \bar{h}_{298\text{K}} - \bar{h}_{500\text{K}} - R_u T)_P - \sum N_R (\bar{h}_f - R_u T)_R \]

since reactants are at the standard reference temperature of 25\textdegree C. From the tables,

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \bar{h}_f ) ( \text{kJ/kmol} )</th>
<th>( \bar{h}_{298\text{K}} ) ( \text{kJ/kmol} )</th>
<th>( \bar{h}_{500\text{K}} ) ( \text{kJ/kmol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>-110,530</td>
<td>8669</td>
<td>14,600</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>0</td>
<td>8682</td>
<td>14,770</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>-393,520</td>
<td>9364</td>
<td>17,678</td>
</tr>
</tbody>
</table>

Substituting,

\[ -Q_{out} = 1(-393,520 + 17,678 - 9364 - 8.314 \times 500) + 2.5(0 + 14,770 - 8682 - 8.314 \times 500) - 3(0 - 8.314 \times 298) - 1(-110,530 - 8.314 \times 298) = -264,095 \text{kJ/kmol CO} \]

or \[ Q_{out} = 264,095 \text{kJ/kmol CO} \]

The final pressure in the tank is determined from

\[ \frac{P_1 \nu}{P_2 \nu} = \frac{N_1 R_u T_1}{N_2 R_u T_2} \rightarrow P_2 = \frac{N_2 T_2}{N_1 T_1} \frac{P_1}{R_u T} = \frac{3.5}{4} \times \frac{500 \text{K}}{298 \text{K}} (2 \text{atm}) = 2.94 \text{ atm} \]

The equilibrium constant for the reaction \( \text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2 \) is \( \ln K_p = 57.62 \), which is much greater than 7. Therefore, it is not realistic to assume that no CO will be present in equilibrium mixture.

**16-93** Using Henry’s law, it is to be shown that the dissolved gases in a liquid can be driven off by heating the liquid.

**Analysis**
Henry’s law is expressed as

\[ \gamma_{i, \text{liquid side}}(0) = \frac{P_{i, \text{gas side}}(0)}{H} \]

Henry’s constant \( H \) increases with temperature, and thus the fraction of gas \( i \) in the liquid \( \gamma_{i, \text{liquid side}} \) decreases. Therefore, heating a liquid will drive off the dissolved gases in a liquid.
A glass of water is left in a room. The mole fraction of the water vapor in the air at the water surface and far from the surface as well as the mole fraction of air in the water near the surface are to be determined when the water and the air are at the same temperature.

**Assumptions**

1. Both the air and water vapor are ideal gases.
2. Air is weakly soluble in water and thus Henry’s law is applicable.

**Properties**

- The saturation pressure of water at 25°C is 3.170 kPa (Table A-4). Henry’s constant for air dissolved in water at 25°C (298 K) is given in Table 16-2 to be \( H = 71,600 \) bar. Molar masses of dry air and water are 29 and 18 kg/kmol, respectively (Table A-1).

**Analysis**

(a) Noting that the relative humidity of air is 70%, the partial pressure of water vapor in the air far from the water surface will be

\[
P_{v,\text{room air}} = \phi P_{\text{sat @ 25°C}} = (0.7)(3.170 \text{ kPa}) = 2.219 \text{ kPa}
\]

Assuming both the air and vapor to be ideal gases, the mole fraction of water vapor in the room air is

\[
y_{vapor} = \frac{P_{vapor}}{P} = \frac{2.219 \text{ kPa}}{100 \text{ kPa}} = \frac{0.0222}{100} = 0.0222 \quad \text{(or 2.22%)}
\]

(b) Noting that air at the water surface is saturated, the partial pressure of water vapor in the air near the surface will simply be the saturation pressure of water at 25°C, \( P_{v,\text{interface}} = P_{\text{sat @ 25°C}} = 3.170 \text{ kPa} \). Then the mole fraction of water vapor in the air at the interface becomes

\[
y_{v,\text{surface}} = \frac{P_{v,\text{surface}}}{P} = \frac{3.170 \text{ kPa}}{100 \text{ kPa}} = \frac{0.0317}{100} = 0.0317 \quad \text{(or 3.17%)}
\]

(c) Noting that the total pressure is 100 kPa, the partial pressure of dry air at the water surface is

\[
P_{\text{air, surface}} = P - P_{v,\text{surface}} = 100 - 3.170 = 96.83 \text{ kPa}
\]

From Henry’s law, the mole fraction of air in the water is determined to be

\[
y_{\text{dry air, liquid side}} = \frac{P_{\text{dry air, gas side}}}{H} = \frac{(96.83 / 100) \text{ bar}}{71,600 \text{ bar}} = 1.35 \times 10^{-5}
\]

**Discussion**

The water cannot remain at the room temperature when the air is not saturated. Therefore, some water will evaporate and the water temperature will drop until a balance is reached between the rate of heat transfer to the water and the rate of evaporation.
A glass of water is left in a room. The mole fraction of the water vapor in the air at the water surface and far from the surface as well as the mole fraction of air in the water near the surface are to be determined when the water and the air are at the same temperature.

Assumptions
1. Both the air and water vapor are ideal gases.
2. Air is weakly soluble in water and thus Henry’s law is applicable.

Properties
The saturation pressure of water at 25°C is 3.170 kPa (Table A-4). Henry’s constant for air dissolved in water at 25°C (298 K) is given in Table 16-2 to be \( H = 71,600 \) bar. Molar masses of dry air and water are 29 and 18 kg/kmol, respectively (Table A-1).

Analysis
(a) Noting that the relative humidity of air is 40\%, the partial pressure of water vapor in the air far from the water surface will be

\[
P_{v, \text{room air}} = \phi P_{\text{sat @ 25°C}} = (0.25)(3.170 \text{ kPa}) = 0.7925 \text{ kPa}
\]

Assuming both the air and vapor to be ideal gases, the mole fraction of water vapor in the room air is

\[
y_{vapor} = \frac{P_{vapor}}{P} = \frac{0.7925 \text{ kPa}}{100 \text{ kPa}} = 0.0079 \quad \text{(or 0.79\%)}
\]

(b) Noting that air at the water surface is saturated, the partial pressure of water vapor in the air near the surface will simply be the saturation pressure of water at 25°C, \( P_{v, \text{interface}} = P_{\text{sat @ 25°C}} = 3.170 \text{ kPa} \). Then the mole fraction of water vapor in the air at the interface becomes

\[
y_{v, \text{surface}} = \frac{P_{v, \text{surface}}}{P} = \frac{3.170 \text{ kPa}}{100 \text{ kPa}} = 0.0317 \quad \text{(or 3.17\%)}
\]

(c) Noting that the total pressure is 100 kPa, the partial pressure of dry air at the water surface is

\[
P_{\text{air, surface}} = P - P_{v, \text{surface}} = 100 - 3.170 = 96.83 \text{ kPa}
\]

From Henry’s law, the mole fraction of air in the water is determined to be

\[
y_{\text{dry air, liquid side}} = \frac{P_{\text{dry air, gas side}}}{H} = \frac{(96.83 / 100) \text{ bar}}{71,600 \text{ bar}} = 1.35 \times 10^{-5}
\]

Discussion
The water cannot remain at the room temperature when the air is not saturated. Therefore, some water will evaporate and the water temperature will drop until a balance is reached between the rate of heat transfer to the water and the rate of evaporation.
A 2-L bottle is filled with carbonated drink that is fully charged (saturated) with CO₂ gas. The volume that the CO₂ gas would occupy if it is released and stored in a container at room conditions is to be determined.

**Assumptions**

1. The liquid drink can be treated as water.
2. Both the CO₂ gas and the water vapor are ideal gases.
3. The CO₂ gas is weakly soluble in water and thus Henry’s law is applicable.

**Properties**

The saturation pressure of water at 17°C is 1.938 kPa (Table A-4). Henry’s constant for CO₂ dissolved in water at 17°C (290 K) is \( H = 1280 \text{ bar} \) (Table 16-2). Molar masses of CO₂ and water are 44.01 and 18.015 kg/kmol, respectively (Table A-1). The gas constant of CO₂ is 0.1889 kPa.m³/kg.K. Also, 1 bar = 100 kPa.

**Analysis**

In the charging station, the CO₂ gas and water vapor mixture above the liquid will form a saturated mixture. Noting that the saturation pressure of water at 17°C is 1.938 kPa, the partial pressure of the CO₂ gas is

\[
P_{\text{CO}_2, \text{gas side}} = P - P_{\text{vapor}} = P - P_{\text{sat at } 17^\circ C} = 600 - 1.938 = 598.06 \text{ kPa} = 5.9806 \text{ bar}
\]

From Henry’s law, the mole fraction of CO₂ in the liquid drink is determined to be

\[
y_{\text{CO}_2, \text{liquid side}} = \frac{P_{\text{CO}_2, \text{gas side}}}{H} = \frac{5.9806 \text{ bar}}{1280 \text{ bar}} = 0.00467
\]

Then the mole fraction of water in the drink becomes

\[
y_{\text{water, liquid side}} = 1 - y_{\text{CO}_2, \text{liquid side}} = 1 - 0.00467 = 0.99533
\]

The mass and mole fractions of a mixture are related to each other by

\[
w_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_L}{M_m}
\]

where the apparent molar mass of the drink (liquid water - CO₂ mixture) is

\[
M_m = \sum y_i M_i = y_{\text{water}} M_{\text{water}} + y_{\text{CO}_2} M_{\text{CO}_2} = 0.99533 \times 18.015 + 0.00467 \times 44.01 = 18.14 \text{ kg/kmol}
\]

Then the mass fraction of dissolved CO₂ in liquid drink becomes

\[
w_{\text{CO}_2, \text{liquid side}} = y_{\text{CO}_2, \text{liquid side}}(0) \frac{M_{\text{CO}_2}}{M_m} = 0.00467 \frac{44.01}{18.14} = 0.0113
\]

Therefore, the mass of dissolved CO₂ in a 2 L ≈ 2 kg drink is

\[
m_{\text{CO}_2} = w_{\text{CO}_2} m_m = 0.0113(2 \text{ kg}) = 0.0226 \text{ kg}
\]

Then the volume occupied by this CO₂ at the room conditions of 20°C and 100 kPa becomes

\[
\mathcal{V} = \frac{mRT}{P} = \frac{(0.0226 \text{ kg})(0.1889 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(293 \text{ K})}{100 \text{ kPa}} = 0.0125 \text{ m}^3 = 12.5 \text{ L}
\]

**Discussion**

Note that the amount of dissolved CO₂ in a 2-L pressurized drink is large enough to fill 6 such bottles at room temperature and pressure. Also, we could simplify the calculations by assuming the molar mass of carbonated drink to be the same as that of water, and take it to be 18 kg/kmol because of the very low mole fraction of CO₂ in the drink.
Ethyl alcohol \( \text{C}_2\text{H}_5\text{OH} \) (gas) is burned in a steady-flow adiabatic combustion chamber with 40 percent excess air. The adiabatic flame temperature of the products is to be determined and the adiabatic flame temperature as a function of the percent excess air is to be plotted.

**Analysis** The complete combustion reaction in this case can be written as

\[
\text{C}_2\text{H}_5\text{OH} \text{(gas)} + (1 + Ex)a_{th} \left[ \text{O}_2 + 3.76\text{N}_2 \right] \rightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O} + (Ex)(a_{th}) \text{O}_2 + f \text{N}_2
\]

where \( a_{th} \) is the stoichiometric coefficient for air. The oxygen balance gives

\[
1 + (1 + Ex)a_{th} \times 2 = 2 \times 2 + 3 \times 1 + (Ex)(a_{th}) \times 2
\]

The reaction equation with products in equilibrium is

\[
\text{C}_2\text{H}_5\text{OH} \text{(gas)} + (1 + Ex)a_{th} \left[ \text{O}_2 + 3.76\text{N}_2 \right] \rightarrow a \text{CO}_2 + b \text{CO} + d \text{H}_2\text{O} + e \text{O}_2 + f \text{N}_2
\]

The coefficients are determined from the mass balances

- Carbon balance: \( 2 = a + b \)
- Hydrogen balance: \( 6 = 2d \rightarrow d = 3 \)
- Oxygen balance: \( 1 + (1 + Ex)a_{th} \times 2 = a \times 2 + b \times 2 + d + e \times 2 \)
- Nitrogen balance: \( (1 + Ex)a_{th} \times 3.76 = f \)

Solving the above equations, we find the coefficients to be

\( Ex = 0.4, a_{th} = 3, a = 1.995, b = 0.004938, d = 3, e = 1.202, f = 15.79 \)

Then, we write the balanced reaction equation as

\[
\text{C}_2\text{H}_5\text{OH} \text{(gas)} + 4.2 \left[ \text{O}_2 + 3.76\text{N}_2 \right] \rightarrow 1.995 \text{CO}_2 + 0.004938 \text{CO} + 3 \text{H}_2\text{O} + 1.202 \text{O}_2 + 15.79 \text{N}_2
\]

Total moles of products at equilibrium are

\( N_{\text{tot}} = 1.995\times0.004938 + 3 + 1.202 + 15.79 = 21.99 \)

The assumed equilibrium reaction is

\( \text{CO}_2 \leftrightarrow \text{CO} + 0.5\text{O}_2 \)

The \( K_p \) value of a reaction at a specified temperature can be determined from the Gibbs function data using

\[
K_p = e^{-\Delta G^*(T)/R_u T} \quad \text{or} \quad \ln K_p = -\Delta G^*(T)/R_u T
\]

where

\[
\Delta G^*(T) = \nu_{\text{CO}} \overline{\gamma}_{\text{CO}}^* (T_{\text{prod}}) + \nu_{\text{O}_2} \overline{\gamma}_{\text{O}_2}^* (T_{\text{prod}}) - \nu_{\text{CO}_2} \overline{\gamma}_{\text{CO}_2}^* (T_{\text{prod}})
\]

and the Gibbs functions are defined as

\[
\overline{\gamma}_{\text{CO}}^* (T_{\text{prod}}) = (\overline{h} - T_{\text{prod}} \overline{\gamma})_{\text{CO}}
\]
\[
\overline{\gamma}_{\text{O}_2}^* (T_{\text{prod}}) = (\overline{h} - T_{\text{prod}} \overline{\gamma})_{\text{O}_2}
\]
\[
\overline{\gamma}_{\text{CO}_2}^* (T_{\text{prod}}) = (\overline{h} - T_{\text{prod}} \overline{\gamma})_{\text{CO}_2}
\]

The equilibrium constant is also given by

\[
K_p = \frac{be^{0.5}}{a} \left( \frac{P}{N_{\text{tot}}} \right)^{1 + 0.5 - 1} = \frac{0.004938(1.202)^{0.5}}{1.995} \left( \frac{1}{21.99} \right)^{0.5} = 0.0005787
\]

A steady flow energy balance gives

\( H_R = H_p \)

where
\[ H_f = h_{f_{\text{fuel,25^\circ C}}} + 4.2h_{O_2,25^\circ C} + 15.79h_{N_2,25^\circ C} \]
\[ = (-235,310 \text{ kJ/kmol}) + 4.2(0) + 15.79(0) = -235,310 \text{ kJ/kmol} \]
\[ H_p = 1.995h_{CO_2,T_{\text{prod}}} + 0.004938h_{CO,T_{\text{prod}}} + 3h_{H_2O,T_{\text{prod}}} + 1.202h_{O_2,T_{\text{prod}}} + 15.79h_{N_2,T_{\text{prod}}} \]

Solving the energy balance equation using EES, we obtain the adiabatic flame temperature to be
\[ T_{\text{prod}} = 1907 \text{ K} \]

The copy of entire EES solution including parametric studies is given next:

"The product temperature is \( T_{\text{prod}} \)"
"The reactant temperature is:"
\[ T_{\text{react}} = 25 + 273.15 \text{ "[K]"} \]
"For adiabatic combustion of 1 kmol of fuel:"
\[ Q_{\text{out}} = 0 \text{ "[kJ]"} \]
\[ \text{PercentEx} = 0 \text{ "Percent excess air"} \]
\[ \text{Ex} = \text{PercentEx}/100 \text{ "EX = % Excess air/100"} \]
\[ P_{\text{prod}} = 101.3 \text{ "[kPa]"} \]
\[ R_u = 8.314 \text{ "[kJ/kmol-K]"} \]
"The complete combustion reaction equation for excess air is:"
\[ \text{C}_2\text{H}_5\text{OH(gas)} + (1+\text{Ex})\text{A}_{\text{th}} \text{(O}_2 + 3.76\text{N}_2) = 2 \text{CO}_2 + 3 \text{H}_2\text{O} + \text{ExA}_{\text{th}} \text{O}_2 + \text{fN}_2 \]
"Oxygen Balance for complete combustion:"
\[ 1 + (1+\text{Ex})\text{A}_{\text{th}}*2 = 2*2 + 3*1 + \text{ExA}_{\text{th}}*2 \]
"The reaction equation for excess air and products in equilibrium is:"
\[ \text{C}_2\text{H}_5\text{OH(gas)} + (1+\text{Ex})\text{A}_{\text{th}} \text{(O}_2 + 3.76\text{N}_2) = a \text{CO}_2 + b \text{CO} + d \text{H}_2\text{O} + e \text{O}_2 + f \text{N}_2 \]
"Carbon Balance:"
\[ 2 = a + b \]
"Hydrogen Balance:"
\[ 6 = 2*d \]
"Oxygen Balance:"
\[ 1 + (1+\text{Ex})\text{A}_{\text{th}}*2 = a*2 + b + d + e*2 \]
"Nitrogen Balance:"
\[ (1+\text{Ex})\text{A}_{\text{th}} * 3.76 = f \]
\[ N_{\text{tot}} = a + b + d + e + f \text{ "Total kilomoles of products at equilibrium"} \]
"The assumed equilibrium reaction is CO2=CO+0.5O2"  
"The following equations provide the specific Gibbs function \( \text{g=h-Ts} \) for each component in the product gases as a function of its temperature, \( T_{\text{prod}} \), at 1 atm pressure, 101.3 kPa" 
\[ \text{g}_{\text{CO}_2} = \text{Enthalpy(CO}_2,\text{T=T}_{\text{prod}}) - \text{T}_{\text{prod}} * \text{Entropy(CO}_2,\text{T=T}_{\text{prod}}, \text{P=101.3}) \]
\[ \text{g}_{\text{CO}} = \text{Enthalpy(CO},\text{T=T}_{\text{prod}}) - \text{T}_{\text{prod}} * \text{Entropy(CO},\text{T=T}_{\text{prod}}, \text{P=101.3}) \]
\[ \text{g}_{\text{O}_2} = \text{Enthalpy(O}_2,\text{T=T}_{\text{prod}}) - \text{T}_{\text{prod}} * \text{Entropy(O}_2,\text{T=T}_{\text{prod}}, \text{P=101.3}) \]
"The standard-state Gibbs function is" 
\[ \text{DELTAG} = 1*\text{g}_{\text{CO}_2} + 0.5*\text{g}_{\text{O}_2} - 1*\text{g}_{\text{CO}} \]
"The equilibrium constant is given by Eq. 15-14."
\[ K_P = \exp(-\text{DELTAG} / (\text{R}_u*\text{T}_{\text{prod}})) \]
\[ P = P_{\text{prod}} / 101.3 \text{ "atm"} \]
"The equilibrium constant is also given by Eq. 15-15."
\[ K_P = (\text{P/}N_{\text{tot}})^{(1+0.5-1)*(b^e*0.5)/(a^1)} \]
\[ \sqrt{\text{P/N}_{\text{tot}}} * b * \sqrt{\text{e}} = K_P * a \]
"The steady-flow energy balance is:"
\[ H_{\text{R}} = Q_{\text{out}} + H_{\text{P}} \]
\[ h_{\text{bar, f}_{\text{C}_2\text{H}_5\text{OH}}} = -235310 \text{ "[kJ/kmol]"} \]
\[ H_R = 1 \times (h_{\text{bar}_f_{\text{C}_2\text{H}_5\text{OH}_{\text{gas}}}}) + (1 + Ex) \times A_{\text{th}} \times \text{ENTHALPY} \left( O_2, T = T_{\text{react}} \right) + (1 + Ex) \times A_{\text{th}} \times 3.76 \times \text{ENTHALPY} \left( N_2, T = T_{\text{react}} \right) \text{ [kJ/kmol]} \]

\[ H_P = a \times \text{ENTHALPY} \left( \text{CO}_2, T = T_{\text{prod}} \right) + b \times \text{ENTHALPY} \left( \text{CO}, T = T_{\text{prod}} \right) + d \times \text{ENTHALPY} \left( \text{H}_2\text{O}, T = T_{\text{prod}} \right) + e \times \text{ENTHALPY} \left( \text{O}_2, T = T_{\text{prod}} \right) + f \times \text{ENTHALPY} \left( \text{N}_2, T = T_{\text{prod}} \right) \text{ [kJ/kmol]} \]

<table>
<thead>
<tr>
<th>a</th>
<th>a_{\text{th}}</th>
<th>b</th>
<th>d</th>
<th>e</th>
<th>f</th>
<th>PercentEx [%]</th>
<th>T_{\text{prod}} [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.922</td>
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<td>3</td>
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</table>
16-98 EES The natural log of the equilibrium constant as a function of temperature between 298 to 3000 K for the equilibrium reaction \( \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \) is to be tabulated and compared to those given in Table A-228.

**Analysis** The \( K_p \) value of a reaction at a specified temperature can be determined from the Gibbs function data using

\[
K_p = e^{-\Delta G^\circ(T)/RT} \quad \text{or} \quad \ln K_p = -\Delta G^\circ(T)/RT
\]

where

\[
\Delta G^\circ(T) = \nu_{\text{CO}_2} \tilde{g}^\circ_{\text{CO}_2}(T) + \nu_{\text{H}_2} \tilde{g}^\circ_{\text{H}_2}(T) - \nu_{\text{CO}} \tilde{g}^\circ_{\text{CO}}(T) - \nu_{\text{H}_2\text{O}} \tilde{g}^\circ_{\text{H}_2\text{O}}(T)
\]

and the Gibbs functions are defined as

\[
\tilde{g}^\circ_{\text{CO}}(T_{\text{prod}}) = (\tilde{h} - T_{\text{prod}} \tilde{v})_{\text{CO}} \\
\tilde{g}^\circ_{\text{H}_2\text{O}}(T_{\text{prod}}) = (\tilde{h} - T_{\text{prod}} \tilde{v})_{\text{H}_2\text{O}} \\
\tilde{g}^\circ_{\text{CO}_2}(T_{\text{prod}}) = (\tilde{h} - T_{\text{prod}} \tilde{v})_{\text{CO}_2} \\
\tilde{g}^\circ_{\text{H}_2}(T_{\text{prod}}) = (\tilde{h} - T_{\text{prod}} \tilde{v})_{\text{H}_2}
\]

The copy of entire EES solution with resulting parametric table is given next:

\[
\{T_{\text{prod}} = 298 \, [\text{K}]\}
\]

\[
\text{R}_{\text{u}} = 8.314 \, [\text{kJ/kmol-}\text{K}] 
\]

"The following equations provide the specific Gibbs function \((g=h-Ts)\) for each component in the product gases as a function of its temperature, \(T_{\text{prod}}\), at 1 atm pressure, 101.3 kPa".

"For \(T_{\text{prod}}:"

\[
g_{\text{CO}} = \text{Enthalpy(CO,T=T_{\text{prod}}) - T_{\text{prod}} * \text{Entropy(CO,T=T_{\text{prod}},P=101.3)}
\]

\[
g_{\text{CO}_2} = \text{Enthalpy(CO}_2,T=T_{\text{prod}}) - T_{\text{prod}} * \text{Entropy(CO}_2,T=T_{\text{prod}},P=101.3)
\]

\[
g_{\text{H}_2} = \text{Enthalpy(H}_2,T=T_{\text{prod}}) - T_{\text{prod}} * \text{Entropy(H}_2,T=T_{\text{prod}},P=101.3)
\]

\[
g_{\text{H}_2\text{O}} = \text{Enthalpy(H}_2\text{O},T=T_{\text{prod}}) - T_{\text{prod}} * \text{Entropy(H}_2\text{O},T=T_{\text{prod}},P=101.3)
\]

"The standard-state Gibbs function is"

\[
\Delta T G = 1^*g_{\text{CO}_2} + 1^*g_{\text{H}_2} - 1^*g_{\text{CO}} - 1^*g_{\text{H}_2\text{O}}
\]

"The equilibrium constant is given by:"

\[
K_p = \text{exp}(-\Delta T G / (R_{\text{u}} T_{\text{prod}}))
\]

\[
\ln K_p = \ln(k_p)
\]

<table>
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<th>( T_{\text{prod}} ) [K]</th>
<th>( \ln K_p )</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>3000</td>
<td>-1.976</td>
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</table>
The percent theoretical air required for the combustion of octane such that the volume fraction of CO in the products is less than 0.1% and the heat transfer are to be determined. Also, the percent theoretical air required for 0.1% CO in the products as a function of product pressure is to be plotted.

**Analysis**

The complete combustion reaction equation for excess air is

$$C_8H_{18} + P_{th}a_{th}[O_2 + 3.76N_2] \rightarrow 8CO_2 + 9H_2O + (P_{th} - 1)a_{th}O_2 + fN_2$$

The oxygen balance is

$$P_{th}a_{th} \times 2 = 8 \times 2 + 9 \times 1 + (P_{th} - 1)a_{th} \times 2$$

The reaction equation for excess air and products in equilibrium is

$$C_8H_{18} + P_{th}a_{th}[O_2 + 3.76N_2] \rightarrow aCO_2 + bCO + dH_2O + eO_2 + fN_2$$

The coefficients are to be determined from the mass balances

- Carbon balance: \(8 = a + b\)
- Hydrogen balance: \(18 = 2d\) \(\rightarrow d = 9\)
- Oxygen balance: \(P_{th}a_{th} \times 2 = a \times 2 + b + d + e \times 2\)
- Nitrogen balance: \(P_{th}a_{th} \times 3.76 = f\)

Volume fraction of CO must be less than 0.1%. That is,

$$y_{CO} = \frac{b}{N_{tot}} = \frac{b}{a + b + d + e + f} = 0.001$$

The assumed equilibrium reaction is

$$CO_2 \rightleftharpoons CO + 0.5O_2$$

The \(K_p\) value of a reaction at a specified temperature can be determined from the Gibbs function data:

- \(\overline{g}_{CO}(T_{prod}) = (\overline{h} - T_{prod}\overline{s})_{CO} = (-53,826) - (2000)(258.48) = -570,781 kJ/kmol\)
- \(\overline{g}_{O_2}(T_{prod}) = (\overline{h} - T_{prod}\overline{s})_{O_2} = (59,193) - (2000)(268.53) = 477,876 kJ/kmol\)
- \(\overline{g}_{CO_2}(T_{prod}) = (\overline{h} - T_{prod}\overline{s})_{CO_2} = (-302,128) - (2000)(309.00) = -920,121 kJ/kmol\)

The enthalpies at 2000 K and entropies at 2000 K and 101.3 kPa are obtained from EES. Substituting,

$$\Delta G^* (T_{prod}) = v_{CO}\overline{g}_{CO}^* (T_{prod}) + v_{O_2}\overline{g}_{O_2}^* (T_{prod}) - v_{CO_2}\overline{g}_{CO_2}^* (T_{prod})$$

$$= l(570,781) + 0.5(477,876) - (-920,121) = 110,402 kJ/kmol$$

$$K_p = \exp\left(\frac{-\Delta G^*(T_{prod})}{R_u T_{prod}}\right) = \exp\left(\frac{-110,402}{(8.314)(2000)}\right) = 0.001308$$

The equilibrium constant is also given by

$$K_p = \frac{be^{0.5}}{a} \left(\frac{P}{N_{tot}}\right)^{1+0.5-1} = \frac{be^{0.5}}{a} \left(\frac{P_{prod} / 101.3}{a + b + d + e + f}\right)^{1+0.5-1}$$

The steady flow energy balance gives

$$H_R = Q_{out} + H_P$$

where
\[ H_R = \tilde{h}_{C8H18} @ 298 K + P_{th}a_{th}\tilde{h}_{O2} @ 298 K + (P_{th}a_{th} \times 3.76)\tilde{h}_{N2} @ 298 K \]
\[ = (-208,459) + P_{th}a_{th}(0) + (P_{th}a_{th} \times 3.76)(0) = -208,459 \text{ kJ/kmol} \]
\[ H_P = a\tilde{h}_{CO2} @ 2000 K + b\tilde{h}_{CO} @ 2000 K + d\tilde{h}_{H2O} @ 2000 K + e\tilde{h}_{O2} @ 2000 K + f\tilde{h}_{N2} @ 2000 K \]
\[ = a(-302,128) + b(-53,826) + d(-169,171) + e(59,193) + f(56,115) \]

The enthalpies are obtained from EES. Solving all the equations simultaneously using EES, we obtain

\[ P_{th} = 1.024, \quad a_{th} = 12.5, \quad a = 7.935, \quad b = 0.06544, \quad d = 9, \quad e = 0.3289, \quad f = 48.11 \]
\[ \text{PercentTh} = P_{th} \times 100 = 1.024 \times 100 = 102.4\% \]
\[ Q_{out} = 995,500 \text{ kJ/kmol C}_8\text{H}_{18} \]

The copy of entire EES solution including parametric studies is given next:

"The product temperature is:"
\[ T_{prod} = 2000 \text{ [K]} \]
"The reactant temperature is:"
\[ T_{reac} = 25+273 \text{ [K]} \]
"PercentTH is Percent theoretical air"
\[ P_{th} = \text{PercentTh}/100 \text{ "Pth = % theoretical air/100"} \]
\[ P_{prod} = 5 \text{ [atm] "convert(atm,kPa)[kPa]"} \]
\[ R_u = 8.314 \text{ [(kJ/kmol-K)]} \]
"The complete combustion reaction equation for excess air is:"
\[ "C8H18+ P_{th}*A_{th} (O2 +3.76N2)=8 CO2 + 9 H2O +(P_{th}-1)*A_{th} O2 + f N2" \]
"Oxygen Balance for complete combustion:"
\[ P_{th}*A_{th}*2=8*2+9*1 + (P_{th}-1)*A_{th}*2 \]
"The reaction equation for excess air and products in equilibrium is:"
\[ "C8H18+ P_{th}*A_{th} (O2 +3.76N2)=a CO2 + b CO+ d H2O + e O2 + f N2" \]
"Carbon Balance:"\[ 8=a + b \]
"Hydrogen Balance:"\[ 18=2*d \]
"Oxygen Balance:"\[ P_{th}*A_{th}*2=a*2+b + d + e*2 \]
"Nitrogen Balance:"\[ P_{th}*A_{th}*3.76 = f \]
\[ N_{tot} = a + b + d + e + f \text{ "Total kilomoles of products at equilibrium"} \]
"The volume faction of CO in the products is to be less than 0.1%. For ideal gas mixtures volume fractions equal mole fractions."
"The mole fraction of CO in the product gases is:"
\[ y_{CO} = 0.001 \]
\[ y_{CO} = b/N_{tot} \]
"The assumed equilibrium reaction is CO2=CO+0.5O2"
"The following equations provide the specific Gibbs function (g=h-Ts) for each component in the product gases as a function of its temperature, T_prod, at 1 atm pressure, 101.3 kPa"
\[ g_{CO2} = \text{Enthalpy}(CO2,T=T_{prod}) - T_{prod} \text{ *Entropy}(CO2,T=T_{prod},P=101.3) \]
\[ g_{CO} = \text{Enthalpy}(CO,T=T_{prod}) - T_{prod} \text{ *Entropy}(CO,T=T_{prod},P=101.3) \]
\[ g_{O2} = \text{Enthalpy}(O2,T=T_{prod}) - T_{prod} \text{ *Entropy}(O2,T=T_{prod},P=101.3) \]
"The standard-state Gibbs function is"
\[ \Delta \text{TAG} = T^*g_{CO} + 0.5g_{O2} - T^*g_{CO2} \]
"The equilibrium constant is given by Eq. 15-14."
\[ K_P = \exp(-\Delta \text{TAG} / (R_u*T_{prod})) \]
\[ P = P_{prod} / 101.3 \text{ atm} \]
"The equilibrium constant is also given by Eq. 15-15."
"K_ P = (P/N_tot)^{(1+0.5-1)}(b^{1+e^{0.5}})/(a^{1})"
\[\sqrt{P/N_{tot}} \times b \times \sqrt{e} = K_ P \times a\]

"The steady-flow energy balance is:"

\[H_R = Q_{out} + H_P\]

\[H_R = 1 \times \text{ENTHALPY}(C8H18,T=T_{reac}) + Pth \times A_{th} \times \text{ENTHALPY}(O2,T=T_{reac}) + Pth \times A_{th} \times 3.76 \times \text{ENTHALPY}(N2,T=T_{reac}) \ [kJ/kmol]\]

\[H_P = a \times \text{ENTHALPY}(CO_2,T=T_{prod}) + b \times \text{ENTHALPY}(CO,T=T_{prod}) + d \times \text{ENTHALPY}(H2O,T=T_{prod}) + e \times \text{ENTHALPY}(O2,T=T_{prod}) + f \times \text{ENTHALPY}(N2,T=T_{prod}) \ [kJ/kmol]\]

<table>
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<tr>
<td>2300</td>
<td>100.3</td>
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</table>

\[\text{P}_{prod} \ [kPa]\]

\[\text{P}_{prod} \ [kPa]\]

\[\%\]

\[\%\]
16-100 If the equilibrium constant for the reaction \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \) is \( K \), the equilibrium constant for the reaction \( 2H_2O \rightarrow 2H_2 + O_2 \) at the same temperature is:

(a) \( \frac{1}{K} \)  
(b) \( \frac{1}{(2K)} \)  
(c) \( 2K \)  
(d) \( K^2 \)  
(e) \( \frac{1}{K^2} \)

Answer (e) \( \frac{1}{K^2} \)

16-101 If the equilibrium constant for the reaction \( CO + \frac{1}{2}O_2 \rightarrow CO_2 \) is \( K \), the equilibrium constant for the reaction \( CO_2 + 3N_2 \rightarrow CO + \frac{1}{2}O_2 + 3N_2 \) at the same temperature is:

(a) \( \frac{1}{K} \)  
(b) \( \frac{1}{(K + 3)} \)  
(c) \( 4K \)  
(d) \( K \)  
(e) \( \frac{1}{K^2} \)

Answer (a) \( \frac{1}{K} \)

16-102 The equilibrium constant for the reaction \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \) at 1 atm and 1500°C is given to be \( K \). Of the reactions given below, all at 1500°C, the reaction that has a different equilibrium constant is:

(a) \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \) at 5 atm,  
(b) \( 2H_2 + O_2 \rightarrow 2H_2O \) at 1 atm,  
(c) \( H_2 + O_2 \rightarrow H_2O + \frac{1}{2}O_2 \) at 2 atm,  
(d) \( H_2 + \frac{1}{2}O_2 + 3N_2 \rightarrow H_2O + 3N_2 \) at 5 atm,  
(e) \( H_2 + \frac{1}{2}O_2 + 3N_2 \rightarrow H_2O + 3N_2 \) at 1 atm,

Answer (b) \( 2H_2 + O_2 \rightarrow 2H_2O \) at 1 atm,

16-103 Of the reactions given below, the reaction whose equilibrium composition at a specified temperature is not affected by pressure is:

(a) \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \)  
(b) \( CO + \frac{1}{2}O_2 \rightarrow CO_2 \)  
(c) \( N_2 + O_2 \rightarrow 2NO \)  
(d) \( N_2 \rightarrow 2N \)  
(e) all of the above.

Answer (c) \( N_2 + O_2 \rightarrow 2NO \)

16-104 Of the reactions given below, the reaction whose number of moles of products increases by the addition of inert gases into the reaction chamber at constant pressure and temperature is:

(a) \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \)  
(b) \( CO + \frac{1}{2}O_2 \rightarrow CO_2 \)  
(c) \( N_2 + O_2 \rightarrow 2NO \)  
(d) \( N_2 \rightarrow 2N \)  
(e) none of the above.

Answer (d) \( N_2 \rightarrow 2N \)
16-105 Moist air is heated to a very high temperature. If the equilibrium composition consists of \( \text{H}_2\text{O}, \text{O}_2, \text{N}_2, \text{OH}, \text{H}_2, \) and \( \text{NO} \), the number of equilibrium constant relations needed to determine the equilibrium composition of the mixture is
(a) 1  (b) 2  (c) 3  (d) 4  (e) 5

\textit{Answer}  (c) 3

16-106 Propane \( \text{C}_3\text{H}_8 \) is burned with air, and the combustion products consist of \( \text{CO}_2, \text{CO}, \text{H}_2\text{O}, \text{O}_2, \text{N}_2, \text{OH}, \text{H}_2, \) and \( \text{NO} \). The number of equilibrium constant relations needed to determine the equilibrium composition of the mixture is
(a) 1  (b) 2  (c) 3  (d) 4  (e) 5

\textit{Answer}  (d) 4

16-107 Consider a gas mixture that consists of three components. The number of independent variables that need to be specified to fix the state of the mixture is
(a) 1  (b) 2  (c) 3  (d) 4  (e) 5

\textit{Answer}  (d) 4

16-108 The value of Henry’s constant for \( \text{CO}_2 \) gas dissolved in water at 290 K is 12.8 MPa. Consider water exposed to air at 100 kPa that contains 3 percent \( \text{CO}_2 \) by volume. Under phase equilibrium conditions, the mole fraction of \( \text{CO}_2 \) gas dissolved in water at 290 K is
(a) \( 2.3\times10^{-4} \)  (b) \( 3.0\times10^{-4} \)  (c) \( 0.80\times10^{-4} \)  (d) \( 2.2\times10^{-4} \)  (e) \( 5.6\times10^{-4} \)

\textit{Answer}  (a) \( 2.3\times10^{-4} \)

\textit{Solution}  Solved by EES Software. Solutions can be verified by copying-and-pasting the following lines on a blank EES screen. (Similar problems and their solutions can be obtained easily by modifying numerical values).

\begin{verbatim}
H=12.8 "MPa"
P=0.1 "MPa"
y_CO2_air=0.03
P_CO2_air=y_CO2_air*P
y_CO2_liquid=P_CO2_air/H

"Some Wrong Solutions with Common Mistakes:"
W1_yCO2=P_CO2_air*H "Multiplying by H instead of dividing by it"
W2_yCO2=P_CO2_air "Taking partial pressure in air"
\end{verbatim}
The solubility of nitrogen gas in rubber at 25°C is 0.00156 kmol/m³-bar. When phase equilibrium is established, the density of nitrogen in a rubber piece placed in a nitrogen gas chamber at 800 kPa is:

(a) 0.012 kg/m³  (b) 0.35 kg/m³  (c) 0.42 kg/m³  (d) 0.56 kg/m³  (e) 0.078 kg/m³

**Answer**  (b) 0.35 kg/m³

**Solution** Solved by EES Software. Solutions can be verified by copying-and-pasting the following lines on a blank EES screen. (Similar problems and their solutions can be obtained easily by modifying numerical values).

```plaintext
T=25 "C"
S=0.00156 "kmol/bar.m^3"
MM_N2=28 "kg/kmol"
S_mass=S*MM_N2 "kg/bar.m^3"
P_N2=8 "bar"
rho_solid=S_mass*P_N2

"Some Wrong Solutions with Common Mistakes:"
W1_density=S*P_N2 "Using solubility per kmol"
```

**16-110 and 16-111 Design and Essay Problems**