Chapter 16

CHEMICAL AND PHASE EQUILIBRIUM

The K$_p$ and Equilibrium Composition of Ideal Gases

16-1C Because when a reacting system involves heat transfer, the increase-in-entropy principle relation requires a knowledge of heat transfer between the system and its surroundings, which is impractical. The equilibrium criteria can be expressed in terms of the properties alone when the Gibbs function is used.

16-2C No, the wooden table is NOT in chemical equilibrium with the air. With proper catalyst, it will reach with the oxygen in the air and burn.

16-3C They are

$$K_p = \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}}, \quad K_p = e^{-\Delta G^*(T)/R_u T} \quad \text{and} \quad K_p = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left(\frac{P}{N_{\text{total}}} \right)^{\Delta \nu}$$

where $\Delta \nu = \nu_C + \nu_D - \nu_A - \nu_B$. The first relation is useful in partial pressure calculations, the second in determining the K_p from gibbs functions, and the last one in equilibrium composition calculations.

16-4C (*a*) This reaction is the reverse of the known CO reaction. The equilibrium constant is then

$$1/K_P$$

(*b*) This reaction is the reverse of the known CO reaction at a different pressure. Since pressure has no effect on the equilibrium constant,

$$1/K_P$$

(*c*) This reaction is the same as the known CO reaction multiplied by 2. The quilibirium constant is then

$$K_P^2$$

(*d*) This is the same as reaction (*c*) occurring at a different pressure. Since pressure has no effect on the equilibrium constant,

$$K_P^2$$

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16-5C (*a*) This reaction is the reverse of the known H_2O reaction. The equilibrium constant is then

$$1/K_P$$

(*b*) This reaction is the reverse of the known H_2O reaction at a different pressure. Since pressure has no effect on the equilibrium constant,

$$1/K_P$$

(*c*) This reaction is the same as the known H_2O reaction multiplied by 3. The quilibirium constant is then

$$K_P^3$$

(*d*) This is the same as reaction (*c*) occurring at a different pressure. Since pressure has no effect on the equilibrium constant,

$$K_P^3$$

16-6C (*a*) No, because K_p depends on temperature only.

(*b*) In general, the total mixture pressure affects the mixture composition. The equilibrium constant for the reaction $N_2 + O_2 \Leftrightarrow 2NO$ can be expressed as

$$K_p = \frac{N_{NO}^{\nu_{NO}}}{N_{N_2}^{\nu_{N2}} N_{O_2}^{\nu_{O2}}} \left(\frac{P}{N_{total}} \right)^{(\nu_{NO} - \nu_{N_2} - \nu_{O_2})}$$

The value of the exponent in this case is 2-1-1 = 0. Therefore, changing the total mixture pressure will have no effect on the number of moles of N_2, O_2 and NO.

16-7C (*a*) The equilibrium constant for the reaction $CO + \frac{1}{2}O_2 \Leftrightarrow CO_2$ can be expressed as

$$K_p = \frac{N_{CO_2}^{\nu_{CO2}}}{N_{CO}^{\nu_{CO}} N_{O_2}^{\nu_{O2}}} \left(\frac{P}{N_{total}} \right)^{(\nu_{CO_2} - \nu_{CO} - \nu_{O_2})}$$

Judging from the values in Table A-28, the K_p value for this reaction decreases as temperature increases. That is, the indicated reaction will be less complete at higher temperatures. Therefore, the number of moles of CO_2 will decrease and the number moles of CO and O_2 will increase as the temperature increases.

(*b*) The value of the exponent in this case is 1-1-0.5=-0.5, which is negative. Thus as the pressure increases, the term in the brackets will decrease. The value of K_p depends on temperature only, and therefore it will not change with pressure. Then to keep the equation balanced, the number of moles of the products (CO_2) must increase, and the number of moles of the reactants (CO, O_2) must decrease.

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16-8C (*a*) The equilibrium constant for the reaction $N_2 \Leftrightarrow 2N$ can be expressed as

$$K_p = \frac{N_{N}^{\nu_N}}{N_{N_2}^{\nu_{N_2}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_N - \nu_{N_2})}$$

Judging from the values in Table A-28, the K_p value for this reaction increases as the temperature increases. That is, the indicated reaction will be more complete at higher temperatures. Therefore, the number of moles of N will increase and the number moles of N_2 will decrease as the temperature increases.

(*b*) The value of the exponent in this case is 2-1 = 1, which is positive. Thus as the pressure increases, the term in the brackets also increases. The value of K_p depends on temperature only, and therefore it will not change with pressure. Then to keep the equation balanced, the number of moles of the products (N) must decrease, and the number of moles of the reactants (N_2) must increase.

16-9C The equilibrium constant for the reaction $CO + \frac{1}{2}O_2 \Leftrightarrow CO_2$ can be expressed as

$$K_p = \frac{N_{CO_2}^{\nu_{CO_2}}}{N_{CO}^{\nu_{CO}} N_{O_2}^{\nu_{O_2}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{CO_2} - \nu_{CO} - \nu_{O_2})}$$

Adding more N_2 (an inert gas) at constant temperature and pressure will increase N_{total} but will have no direct effect on other terms. Then to keep the equation balanced, the number of moles of the products (CO_2) must increase, and the number of moles of the reactants (CO, O_2) must decrease.

16-10C The values of the equilibrium constants for each dissociation reaction at 3000 K are, from Table A-28,

$$N_2 \Leftrightarrow 2N \Leftrightarrow \ln K_p = -22.359$$

$$H_2 \Leftrightarrow 2H \Leftrightarrow \ln K_p = -3.685 \quad \text{(greater than - 22.359)}$$

Thus H_2 is more likely to dissociate than N_2.

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16-11 The mole fractions of the constituents of an ideal gas mixture is given. The Gibbs function of the CO in this mixture at the given mixture pressure and temperature is to be determined.

Analysis From Tables A-21 and A-26, at 1 atm pressure,

$$\begin{aligned}\bar{g}^*(800\text{ K}, 1\text{ atm}) &= \bar{g}_f^o + \Delta\left[\bar{h}(T) - T\bar{s}^o(T)\right]\\ &= -137{,}150 + (23{,}844 - 800\times 227.162) - (8669 - 298\times 197.543)\\ &= -244{,}837\text{ kJ/kmol}\end{aligned}$$

10% CO_2
60% H_2O
30% CO
10 atm
800 K

The partial pressure of CO is

$$P_{\text{CO}} = y_{\text{CO}}P = (0.30)(10\text{ atm}) = 3\text{ atm}$$

The Gibbs function of CO at 800 K and 3 atm is

$$\begin{aligned}\bar{g}(800\text{ K}, 3\text{ atm}) &= \bar{g}^*(800\text{ K}, 1\text{ atm}) + R_u T\ln P_{\text{CO}}\\ &= -244{,}837\text{ kJ/kmol} + (8.314\text{ kJ/kmol})(800\text{ K})\ln(3\text{ atm})\\ &= \mathbf{-237{,}530\text{ kJ/kmol}}\end{aligned}$$

16-12 The partial pressures of the constituents of an ideal gas mixture is given. The Gibbs function of the nitrogen in this mixture at the given mixture pressure and temperature is to be determined.

Analysis The partial pressure of nitrogen is

$$P_{\text{N2}} = 130\text{ kPa} = (130/101.325) = 1.283\text{ atm}$$

N_2 ,CO_2, NO

P_{N2} = 130 kPa
298 K

The Gibbs function of nitrogen at 298 K and 3 atm is

$$\begin{aligned}\bar{g}(800\text{ K}, 3\text{ atm}) &= \bar{g}^*(298\text{ K}, 1\text{ atm}) + R_u T\ln P_{\text{N2}}\\ &= 0 + (8.314\text{ kJ/kmol})(298\text{ K})\ln(1.283\text{ atm})\\ &= \mathbf{617.4\text{ kJ/kmol}}\end{aligned}$$

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16-13E The equilibrium constant of the reaction $H_2O \Leftrightarrow H_2 + \frac{1}{2}O_2$ is to be determined using Gibbs function.

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

$$K_p = e^{-\Delta G^*(T)/R_uT} \quad \text{or} \quad \ln K_p = -\Delta G^*(T)/R_uT$$

$H_2O \leftrightarrow H_2 + ½O_2$

1440 R

where

$$\Delta G^*(T) = \nu_{H2}\bar{g}^*_{H2}(T) + \nu_{O2}\bar{g}^*_{O2}(T) - \nu_{H2O}\bar{g}^*_{H2O}(T)$$

At 1440 R,

$$\begin{aligned}
\Delta G^*(T) &= \nu_{H2}\bar{g}^*_{H2}(T) + \nu_{O2}\bar{g}^*_{O2}(T) - \nu_{H2O}\bar{g}^*_{H2O}(T) \\
&= \nu_{H2}(\bar{h} - T\bar{s})_{H2} + \nu_{O2}(\bar{h} - T\bar{s})_{O2} - \nu_{H2O}(\bar{h} - T\bar{s})_{H2O} \\
&= \nu_{H2}[(\bar{h}_f + \bar{h}_{1440} - \bar{h}_{537}) - T\bar{s}]_{H2} \\
&\quad + \nu_{O2}[(\bar{h}_f + \bar{h}_{1440} - \bar{h}_{537}) - T\bar{s}]_{O2} \\
&\quad - \nu_{H2O}[(\bar{h}_f + \bar{h}_{1440} - \bar{h}_{537}) - T\bar{s}]_{H2O} \\
&= 1 \times (0 + 9956.9 - 3640.3 - 1440 \times 38.079) \\
&\quad + 0.5 \times (0 + 10{,}532.0 - 3725.1 - 1440 \times 56.326) \\
&\quad - 1 \times (-104{,}040 + 11{,}933.4 - 4258 - 1440 \times 53.428) \\
&= 87{,}632 \text{ Btu/lbmol}
\end{aligned}$$

Substituting,

$$\ln K_p = -(87{,}632 \text{ Btu/lbmol})/[(1.986 \text{ Btu/lbmol.R})(1440 \text{ R})] = \mathbf{-30.64}$$

or

$$K_p = \mathbf{4.93 \times 10^{-14}} \quad (\text{Table A-28}: \ln K_p = -34.97 \text{ by interpolation})$$

At 3960 R,

$$\begin{aligned}
\Delta G^*(T) &= \nu_{H2}\bar{g}^*_{H2}(T) + \nu_{O2}\bar{g}^*_{O2}(T) - \nu_{H2O}\bar{g}^*_{H2O}(T) \\
&= \nu_{H2}(\bar{h} - T\bar{s})_{H2} + \nu_{O2}(\bar{h} - T\bar{s})_{O_2} - \nu_{H2O}(\bar{h} - T\bar{s})_{H2O} \\
&= \nu_{H2}[(\bar{h}_f + \bar{h}_{3960} - \bar{h}_{537}) - T\bar{s}]_{H2} \\
&\quad + \nu_{O2}[(\bar{h}_f + \bar{h}_{3960} - \bar{h}_{537}) - T\bar{s}]_{O2} \\
&\quad - \nu_{H2O}[(\bar{h}_f + \bar{h}_{3960} - \bar{h}_{537}) - T\bar{s}]_{H2O} \\
&= 1 \times (0 + 29{,}370.5 - 3640.3 - 3960 \times 45.765) \\
&\quad + 0.5 \times (0 + 32{,}441 - 3725.1 - 3960 \times 65.032) \\
&\quad - 1 \times (-104{,}040 + 39{,}989 - 4258 - 3960 \times 64.402) \\
&= 53{,}436 \text{ Btu/lbmol}
\end{aligned}$$

Substituting,

$$\ln K_p = -(53{,}436 \text{ Btu/lbmol})/[(1.986 \text{ Btu/lbmol.R})(3960 \text{ R})] = \mathbf{-6.79}$$

or $\quad K_p = \mathbf{1.125 \times 10^{-3}} \quad (\text{Table A-28}: \ln K_p = -6.768)$

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16-14 The reaction $2H_2O \Leftrightarrow 2H_2 + O_2$ is considered. The mole fractions of the hydrogen and oxygen produced when this reaction occurs at 4000 K and 10 kPa 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 The stoichiometric and actual reactions in this case are

Stoichiometric: $2H_2O \Leftrightarrow 2H_2 + O_2$ (thus $\nu_{H2O} = 2,\ \nu_{H2} = 2,\ \text{and}\ \nu_{O2} = 1$)

Actual: $2H_2O \longrightarrow \underbrace{xH_2O}_{\text{react.}} + \underbrace{yH_2 + zO_2}_{\text{products}}$

2H₂O
4000 K
10 kPa

H balance: $4 = 2x + 2y \longrightarrow y = 2 - x$

O balance: $2 = x + 2z \longrightarrow z = 1 - 0.5x$

Total number of moles: $N_{\text{total}} = x + y + z = 3 - 0.5x$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{H2}^{\nu_{H2}} N_{O2}^{\nu_{O2}}}{N_{H2O}^{\nu_{H2O}}} \left(\frac{P}{N_{\text{total}}} \right)^{(\nu_{H2} + \nu_{O2} - \nu_{H2O})}$$

From Table A-28, $\ln K_p = -0.542$ at $4000\ \text{K}$. Since the stoichiometric reaction being considered is double this reaction,

$$K_p = \exp(-2 \times 0.542) = 0.3382$$

Substituting,

$$0.3382 = \frac{(2-x)^2 (1-0.5x)}{x^2} \left(\frac{10/101.325}{3-0.5x} \right)^{2+1-2}$$

Solving for x,

$$x = 0.4446$$

Then,

$$y = 2 - x = 1.555$$

$$z = 1 - 0.5x = 0.7777$$

Therefore, the equilibrium composition of the mixture at 4000 K and 10 kPa is

$$0.4446\, H_2O + 1.555\, H_2 + 0.7777\, O_2$$

The mole fractions of hydrogen and oxygen produced are

$$y_{H2} = \frac{N_{H2}}{N_{\text{total}}} = \frac{1.555}{3 - 0.5 \times 0.4446} = \frac{1.555}{2.778} = \mathbf{0.560}$$

$$y_{O2} = \frac{N_{O2}}{N_{\text{total}}} = \frac{0.7777}{2.778} = \mathbf{0.280}$$

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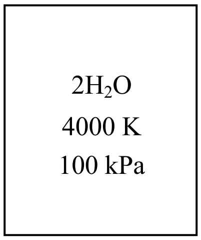
16-15 The reaction $2H_2O \Leftrightarrow 2H_2 + O_2$ is considered. The mole fractions of hydrogen gas produced is to be determined at 100 kPa and compared to that at 10 kPa.

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

Analysis The stoichiometric and actual reactions in this case are

Stoichiometric: $2H_2O \Leftrightarrow 2H_2 + O_2$ (thus $\nu_{H2O} = 2,\ \nu_{H2} = 2,$ and $\nu_{O2} = 1$)

Actual: $2H_2O \longrightarrow \underbrace{xH_2O}_{\text{react.}} + \underbrace{yH_2 + zO_2}_{\text{products}}$



H balance: $4 = 2x + 2y \longrightarrow y = 2 - x$

O balance: $2 = x + 2z \longrightarrow z = 1 - 0.5x$

Total number of moles: $N_{\text{total}} = x + y + z = 3 - 0.5x$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{H2}^{\nu_{H2}} N_{O2}^{\nu_{O2}}}{N_{H2O}^{\nu_{H2O}}} \left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{H2}+\nu_{O2}-\nu_{H2O})}$$

From Table A-28, $\ln K_p = -0.542$ at 4000 K. Since the stoichiometric reaction being considered is double this reaction,

$$K_p = \exp(-2 \times 0.542) = 0.3382$$

Substituting,

$$0.3382 = \frac{(2-x)^2(1-0.5x)}{x^2}\left(\frac{100/101.325}{3-0.5x}\right)^{2+1-2}$$

Solving for x,

$$x = 0.8870$$

Then,

$$y = 2 - x = 1.113$$

$$z = 1 - 0.5x = 0.5565$$

Therefore, the equilibrium composition of the mixture at 4000 K and 100 kPa is

$$0.8870\,H_2O + 1.113\,H_2 + 0.5565\,O_2$$

That is, there are **1.113 kmol** of hydrogen gas. The mole number of hydrogen at 10 kPa reaction pressure was obtained in the previous problem to be **1.555 kmol**. Therefore, the amount of hydrogen gas produced has decreased.

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16-16 The reaction $2H_2O \Leftrightarrow 2H_2 + O_2$ is considered. The mole number of hydrogen gas produced is to be determined if inert nitrogen is mixed with water vapor is to be determined and compared to the case with no inert nitrogen.

Assumptions **1** The equilibrium composition consists of H_2O, H_2, O_2, and N_2. **2** The constituents of the mixture are ideal gases.

Analysis The stoichiometric and actual reactions in this case are

Stoichiometric: $2H_2O \Leftrightarrow 2H_2 + O_2$ (thus $\nu_{H2O} = 2,\ \nu_{H2} = 2,\ \text{and}\ \nu_{O2} = 1$)

Actual: $$2H_2O + 0.5N_2 \longrightarrow \underbrace{xH_2O}_{\text{react.}} + \underbrace{yH_2 + zO_2}_{\text{products}} + \underbrace{0.5N_2}_{\text{inert}}$$

$2H_2O$, $0.5N_2$
4000 K
10 kPa

H balance: $4 = 2x + 2y \longrightarrow y = 2 - x$

O balance: $2 = x + 2z \longrightarrow z = 1 - 0.5x$

Total number of moles: $N_{\text{total}} = x + y + z + 0.5 = 3.5 - 0.5x$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{H2}^{\nu_{H2}} N_{O2}^{\nu_{O2}}}{N_{H2O}^{\nu_{H2O}}} \left(\frac{P}{N_{\text{total}}} \right)^{(\nu_{H2} + \nu_{O2} - \nu_{H2O})}$$

From Table A-28, $\ln K_p = -0.542$ at $4000\ \text{K}$. Since the stoichiometric reaction being considered is double this reaction,

$$K_p = \exp(-2 \times 0.542) = 0.3382$$

Substituting,

$$0.3382 = \frac{(2-x)^2 (1-0.5x)}{x^2} \left(\frac{10/101.325}{3.5 - 0.5x} \right)^{2+1-2}$$

Solving for x,

$$x = 0.4187$$

Then,

$$y = 2 - x = 1.581$$

$$z = 1 - 0.5x = 0.7907$$

Therefore, the equilibrium composition of the mixture at 4000 K and 10 kPa is

$$0.4187\ H_2O + 1.581\ H_2 + 0.7907\ O_2$$

That is, there are **1.581 kmol** of hydrogen gas. The mole number of hydrogen without inert nitrogen case was obtained in Prob. 16-14 to be **1.555 kmol**. Therefore, the amount of hydrogen gas produced has increased.

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16-17E The temperature at which 15 percent of diatomic oxygen dissociates into monatomic oxygen at two pressures is to be determined.

Assumptions **1** The equilibrium composition consists of O_2 and O. **2** The constituents of the mixture are ideal gases.

Analysis (*a*) The stoichiometric and actual reactions can be written as

Stoichiometric: $O_2 \Leftrightarrow 2O$ (thus $\nu_{O2} = 1$ and $\nu_O = 2$)

Actual: $O_2 \Leftrightarrow \underbrace{0.85O_2}_{\text{react.}} + \underbrace{0.3O}_{\text{prod.}}$

$O_2 \leftrightarrow 2O$
15 %
3 psia

The equilibrium constant K_p can be determined from

$$K_p = \frac{N_O^{\nu_O}}{N_{O2}^{\nu_{O2}}}\left(\frac{P}{N_{\text{total}}}\right)^{\nu_O-\nu_{O2}} = \frac{0.3^2}{0.85}\left(\frac{3/14.696}{0.85+0.3}\right)^{2-1} = 0.01880$$

and

$$\ln K_p = -3.974$$

From Table A-28, the temperature corresponding to this $\ln K_p$ value is

T = 3060 K = **5508 R**

(*b*) At 100 psia,

$$K_p = \frac{N_O^{\nu_O}}{N_{O2}^{\nu_{O2}}}\left(\frac{P}{N_{\text{total}}}\right)^{\nu_O-\nu_{O2}} = \frac{0.3^2}{0.85}\left(\frac{100/14.696}{0.85+0.3}\right)^{2-1} = 0.6265$$

$$\ln K_p = -0.4676$$

From Table A-28, the temperature corresponding to this $\ln K_p$ value is

T = 3701 K = **6662 R**

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16-18 The dissociation reaction $CO_2 \Leftrightarrow CO + O$ is considered. The composition of the products at given pressure and temperature is to be determined.

Assumptions **1** The equilibrium composition consists of CO_2, CO, and O. **2** The constituents of the mixture are ideal gases.

Analysis For the stoichiometric reaction $CO_2 \Leftrightarrow CO + \frac{1}{2}O_2$, from Table A-28, at 2500 K

$$\ln K_p = -3.331$$

For the oxygen dissociation reaction $0.5O_2 \Leftrightarrow O$, from Table A-28, at 2500 K,

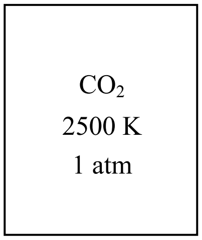
$$\ln K_p = -8.509/2 = -4.255$$

For the desired stoichiometric reaction $CO_2 \Leftrightarrow CO + O$ (thus $\nu_{CO2} = 1,\ \nu_{CO} = 1$ and $\nu_O = 1$),

$$\ln K_p = -3.331 - 4.255 = -7.586$$

and

$$K_p = \exp(-7.586) = 0.0005075$$



Actual: $CO_2 \longrightarrow \underbrace{xCO_2}_{\text{react.}} + \underbrace{yCO + zO}_{\text{products}}$

C balance: $1 = x + y \longrightarrow y = 1 - x$

O balance: $2 = 2x + y + z \longrightarrow z = 1 - x$

Total number of moles: $N_{total} = x + y + z = 2 - x$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{CO}^{\nu_{CO}} N_O^{\nu_O}}{N_{CO2}^{\nu_{CO2}}} \left(\frac{P}{N_{total}} \right)^{\nu_{CO} + \nu_O - \nu_{CO2}}$$

Substituting,

$$0.0005075 = \frac{(1-x)(1-x)}{x} \left(\frac{1}{2-x} \right)^{1+1-1}$$

Solving for x,

$$x = 0.9775$$

Then,

$$y = 1 - x = 0.0225$$

$$z = 1 - x = 0.0225$$

Therefore, the equilibrium composition of the mixture at 2500 K and 1 atm is

$$\mathbf{0.9775\ CO_2 + 0.0225\ CO + 0.0225\ O}$$

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16-19 The dissociation reaction $CO_2 \Leftrightarrow CO + O$ is considered. The composition of the products at given pressure and temperature is to be determined when nitrogen is added to carbon dioxide.

Assumptions **1** The equilibrium composition consists of CO_2, CO, O, and N_2. **2** The constituents of the mixture are ideal gases.

Analysis For the stoichiometric reaction $CO_2 \Leftrightarrow CO + \frac{1}{2}O_2$, from Table A-28, at 2500 K

$$\ln K_p = -3.331$$

For the oxygen dissociation reaction $0.5O_2 \Leftrightarrow O$, from Table A-28, at 2500 K,

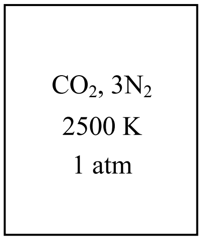
$$\ln K_p = -8.509/2 = -4.255$$

For the desired stoichiometric reaction $CO_2 \Leftrightarrow CO + O$ (thus $\nu_{CO2} = 1$, $\nu_{CO} = 1$ and $\nu_O = 1$),

$$\ln K_p = -3.331 - 4.255 = -7.586$$

and

$$K_p = \exp(-7.586) = 0.0005075$$



Actual: $$CO_2 + 3N_2 \longrightarrow \underbrace{xCO_2}_{\text{react.}} + \underbrace{yCO + zO}_{\text{products}} + \underbrace{3N_2}_{\text{inert}}$$

C balance: $1 = x + y \longrightarrow y = 1 - x$

O balance: $2 = 2x + y + z \longrightarrow z = 1 - x$

Total number of moles: $N_{total} = x + y + z + 3 = 5 - x$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{CO}^{\nu_{CO}} N_O^{\nu_O}}{N_{CO2}^{\nu_{CO2}}} \left(\frac{P}{N_{total}} \right)^{\nu_{CO} + \nu_O - \nu_{CO2}}$$

Substituting,

$$0.0005075 = \frac{(1-x)(1-x)}{x} \left(\frac{1}{5-x} \right)^{1+1-1}$$

Solving for *x*,

$$x = 0.9557$$

Then,

$$y = 1 - x = 0.0443$$

$$z = 1 - x = 0.0443$$

Therefore, the equilibrium composition of the mixture at 2500 K and 1 atm is

$$\mathbf{0.9557\ CO_2 + 0.0443\ CO + 0.0443\ O + 3N_2}$$

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16-20 It is to be shown that as long as the extent of the reaction, α, for the disassociation reaction $X_2 \Leftrightarrow 2X$ is smaller than one, α is given by $\alpha = \sqrt{\dfrac{K_P}{4+K_P}}$

Assumptions The reaction occurs at the reference temperature.

Analysis The stoichiometric and actual reactions can be written as

Stoichiometric: $\mathrm{X}_2 \Leftrightarrow 2\mathrm{X}$ (thus $\nu_{\mathrm{X2}} = 1$ and $\nu_{\mathrm{X}} = 2$)

Actual: $\mathrm{X}_2 \Leftrightarrow \underbrace{(1-\alpha)\mathrm{X}_2}_{\text{react.}} + \underbrace{2\alpha X}_{\text{prod.}}$

The equilibrium constant K_p is given by

$$K_p = \frac{N_{\mathrm{X}}^{\nu_{\mathrm{X}}}}{N_{\mathrm{X2}}^{\nu_{\mathrm{X2}}}}\left(\frac{P}{N_{\text{total}}}\right)^{\nu_{\mathrm{X}}-\nu_{\mathrm{X2}}} = \frac{(2\alpha)^2}{(1-\alpha)}\left(\frac{1}{\alpha+1}\right)^{2-1} = \frac{4\alpha^2}{(1-\alpha)(1+\alpha)}$$

Solving this expression for α gives

$$\alpha = \sqrt{\frac{K_P}{4+K_P}}$$

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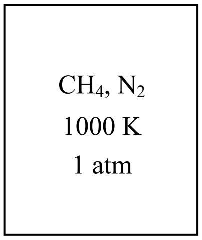
16-21 A gaseous mixture consisting of methane and nitrogen is heated. The equilibrium composition (by mole fraction) of the resulting mixture is to be determined.

Assumptions **1** The equilibrium composition consists of CH_4, C, H_2, and N_2. **2** The constituents of the mixture are ideal gases.

Analysis The stoichiometric and actual reactions in this case are

Stoichiometric: $CH_4 \Leftrightarrow C + 2H_2$ (thus $\nu_{CH4} = 1,\ \nu_C = 1,\ \text{and}\ \nu_{H2} = 2$)

Actual: $$CH_4 + N_2 \longrightarrow \underbrace{xCH_4}_{\text{react.}} + \underbrace{yC + zH_2}_{\text{products}} + \underbrace{N_2}_{\text{inert}}$$



C balance: $1 = x + y \longrightarrow y = 1 - x$

H balance: $4 = 4x + 2z \longrightarrow z = 2 - 2x$

Total number of moles: $N_{total} = x + y + z + 1 = 4 - 2x$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{CH4}^{\nu_{CH4}}}{N_C^{\nu_C} N_{H2}^{\nu_{H2}}} \left(\frac{P}{N_{total}} \right)^{\nu_{CH4} - \nu_C - \nu_{H2}}$$

From the problem statement at 1000 K, $\ln K_p = 2.328$. Then,

$$K_p = \exp(2.328) = 10.257$$

For the reverse reaction that we consider,

$$K_p = 1/10.257 = 0.09749$$

Substituting,

$$0.09749 = \frac{x}{(1-x)(2-2x)^2} \left(\frac{1}{4-2x} \right)^{1-1-2}$$

Solving for x,

$$x = 0.02325$$

Then,

$$y = 1 - x = 0.9768$$

$$z = 2 - 2x = 1.9535$$

Therefore, the equilibrium composition of the mixture at 1000 K and 1 atm is

$$0.02325\,CH_4 + 0.9768\,C + 1.9535\,H_2 + 1\,N_2$$

The mole fractions are

$$y_{CH4} = \frac{N_{CH4}}{N_{total}} = \frac{0.02325}{4 - 2 \times 0.02325} = \frac{0.02325}{3.954} = \mathbf{0.0059}$$

$$y_C = \frac{N_C}{N_{total}} = \frac{0.9768}{3.954} = \mathbf{0.2470}$$

$$y_{H2} = \frac{N_{H2}}{N_{total}} = \frac{1.9535}{3.954} = \mathbf{0.4941}$$

$$y_{N2} = \frac{N_{N2}}{N_{total}} = \frac{1}{3.954} = \mathbf{0.2529}$$

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16-22 The reaction $N_2 + O_2 \Leftrightarrow 2NO$ is considered. The equilibrium mole fraction of NO 1000 K and 1 atm is to be determined.

Assumptions **1** The equilibrium composition consists of N_2, O_2, and NO. **2** The constituents of the mixture are ideal gases.

Analysis The stoichiometric and actual reactions in this case are

Stoichiometric: $N_2 + O_2 \Leftrightarrow 2NO$ (thus $\nu_{N2} = 1$, $\nu_{O2} = 1$, and $\nu_{NO} = 2$)

Actual: $N_2 + O_2 \longrightarrow \underbrace{xN_2 + yO_2}_{\text{react.}} + \underbrace{zNO}_{\text{products}}$

N balance: $2 = 2x + z \longrightarrow z = 2 - 2x$

O balance: $2 = 2y + z \longrightarrow y = x$

Total number of moles: $N_{\text{total}} = x + y + z = 2$

N_2, O_2
1000 K
1 atm

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{NO}^{\nu_{NO}}}{N_{N2}^{\nu_{N2}} N_{O2}^{\nu_{O2}}} \left(\frac{P}{N_{\text{total}}} \right)^{(\nu_{NO} - \nu_{N2} - \nu_{O2})}$$

From Table A-28, at 1000 K, $\ln K_p = -9.388$. Since the stoichiometric reaction being considered is double this reaction,

$$K_p = \exp(-2 \times 9.388) = 7.009 \times 10^{-9}$$

Substituting,

$$7.009 \times 10^{-9} = \frac{(2 - 2x)^2}{x^2} \left(\frac{1}{2} \right)^{2-1-1}$$

Solving for *x*,

$$x = 0.999958$$

Then,

$$y = x = 0.999958$$

$$z = 2 - 2x = 8.4 \times 10^{-5}$$

Therefore, the equilibrium composition of the mixture at 1000 K and 1 atm is

$$0.999958\, N_2 + 0.999958\, O_2 + 8.4 \times 10^{-5}\ NO$$

The mole fraction of NO is then

$$y_{NO} = \frac{N_{NO}}{N_{\text{total}}} = \frac{8.4 \times 10^{-5}}{2} = \mathbf{4.2 \times 10^{-5}} \quad \text{(42 parts per million)}$$

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16-23 Oxygen is heated from a specified state to another state. The amount of heat required is to be determined without and with dissociation cases.

Assumptions **1** The equilibrium composition consists of O_2 and O. **2** The constituents of the mixture are ideal gases.

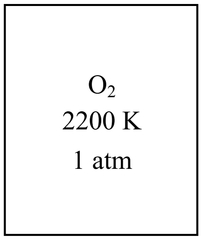
Analysis (*a*) Obtaining oxygen properties from table A-19, an energy balance gives

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer}\\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,}\\ \text{potential, etc. energies}}}$$

$$q_{\text{in}} = \bar{u}_2 - \bar{u}_1$$

$$= 57{,}192 - 6203$$

$$= \mathbf{50{,}989\ kJ/kmol}$$



(*b*) The stoichiometric and actual reactions in this case are

Stoichiometric: $O_2 \Leftrightarrow 2O$ (thus $\nu_{O2} = 1$ and $\nu_O = 2$)

Actual: $O_2 \longrightarrow \underbrace{xO_2}_{\text{react.}} + \underbrace{yO}_{\text{products}}$

O balance: $2 = 2x + y \longrightarrow y = 2 - 2x$

Total number of moles: $N_{\text{total}} = x + y = 2 - x$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_O^{\nu_O}}{N_{O2}^{\nu_{O2}}}\left(\frac{P}{N_{\text{total}}}\right)^{\nu_O - \nu_{O2}}$$

From Table A-28, at 2200 K, $\ln K_p = -11.827$. Then,

$$K_p = \exp(-11.827) = 7.305 \times 10^{-6}$$

Substituting,

$$7.305 \times 10^{-6} = \frac{(2-2x)^2}{x}\left(\frac{1}{2-x}\right)^{2-1}$$

Solving for *x*,

$$x = 0.99865$$

Then,

$$y = 2 - 2x = 0.0027$$

Therefore, the equilibrium composition of the mixture at 2200 K and 1 atm is

$$0.99865\,O_2 + 0.0027\,O$$

Hence, the oxygen ions are negligible and the result is same as that in part (a),

$$q_{\text{in}} = \mathbf{50{,}989\ kJ/kmol}$$

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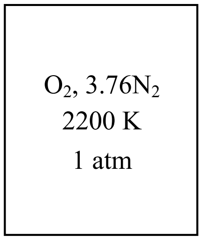
16-24 Air is heated from a specified state to another state. The amount of heat required is to be determined without and with dissociation cases.

Assumptions **1** The equilibrium composition consists of O_2 and O, and N_2. **2** The constituents of the mixture are ideal gases.

Analysis (*a*) Obtaining air properties from table A-17, an energy balance gives

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer}\\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,}\\ \text{potential, etc. energies}}}$$

$$\begin{aligned} q_{\text{in}} &= u_2 - u_1 \\ &= 1872.4 - 212.64 \\ &= \mathbf{1660\ kJ/kg} \end{aligned}$$



(*b*) The stoichiometric and actual reactions in this case are

Stoichiometric: $O_2 \Leftrightarrow 2O$ (thus $\nu_{O2} = 1$ and $\nu_O = 2$)

Actual: $O_2 + 3.76N_2 \longrightarrow \underbrace{xO_2}_{\text{react.}} + \underbrace{yO}_{\text{products}} + \underbrace{3.76N_2}_{\text{inert}}$

O balance: $2 = 2x + y \longrightarrow y = 2 - 2x$

Total number of moles: $N_{\text{total}} = x + y + 3.76 = 5.76 - x$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_O^{\nu_O}}{N_{O2}^{\nu_{O2}}}\left(\frac{P}{N_{\text{total}}}\right)^{\nu_O - \nu_{O2}}$$

From Table A-28, at 2200 K, $\ln K_p = -11.827$. Then,

$$K_p = \exp(-11.827) = 7.305 \times 10^{-6}$$

Substituting,

$$7.305 \times 10^{-6} = \frac{(2-2x)^2}{x}\left(\frac{1}{5.76 - x}\right)^{2-1}$$

Solving for *x*,

$$x = 0.99706$$

Then,

$$y = 2 - 2x = 0.00588$$

Therefore, the equilibrium composition of the mixture at 2200 K and 1 atm is

$$0.99706\,O_2 + 0.00588\,O + 3.76\,N_2$$

Hence, the atomic oxygen is negligible and the result is same as that in part (a),

$$q_{\text{in}} = \mathbf{1660\ kJ/kg}$$

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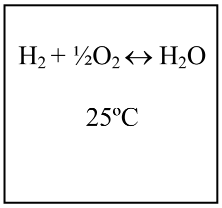
16-25 The equilibrium constant of the reaction $H_2 + 1/2O_2 \leftrightarrow H_2O$ is listed in Table A-28 at different temperatures. The data are to be verified at two temperatures using Gibbs function data.

Analysis (*a*) 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

$$\Delta G^*(T) = \nu_{H_2O}\bar{g}^*_{H_2O}(T) - \nu_{H_2}\bar{g}^*_{H_2}(T) - \nu_{O_2}\bar{g}^*_{O_2}(T)$$

At 25°C,

$$\Delta G^*(T) = 1(-228{,}590) - 1(0) - 0.5(0) = -228{,}590 \text{ kJ / kmol}$$

Substituting,

$$\ln K_p = -(-228{,}590 \text{ kJ/kmol})/[(8.314 \text{ kJ/kmol}\cdot\text{K})(298 \text{ K})] = 92.26$$

or

$$K_p = \mathbf{1.12 \times 10^{40}} \quad (\text{Table A-28: } \ln K_p = 92.21)$$

(*b*) At 2000 K,

$$\begin{aligned}
\Delta G^*(T) &= \nu_{H_2O}\bar{g}^*_{H_2O}(T) - \nu_{H_2}\bar{g}^*_{H_2}(T) - \nu_{O_2}\bar{g}^*_{O_2}(T) \\
&= \nu_{H_2O}(\bar{h} - T\bar{s})_{H_2O} - \nu_{H_2}(\bar{h} - T\bar{s})_{H_2} - \nu_{O_2}(\bar{h} - T\bar{s})_{O_2} \\
&= \nu_{H_2O}[(\bar{h}_f + \bar{h}_{2000} - \bar{h}_{298}) - T\bar{s}]_{H_2O} \\
&\quad - \nu_{H_2}[(\bar{h}_f + \bar{h}_{2000} - \bar{h}_{298}) - T\bar{s}]_{H_2} \\
&\quad - \nu_{O_2}[(\bar{h}_f + \bar{h}_{2000} - \bar{h}_{298}) - T\bar{s}]_{O_2} \\
&= 1 \times (-241{,}820 + 82{,}593 - 9904 - 2000 \times 264.571) \\
&\quad - 1 \times (0 + 61{,}400 - 8468 - 2000 \times 188.297) \\
&\quad - 0.5 \times (0 + 67{,}881 - 8682) - 2000 \times 268.655) \\
&= -135{,}556 \text{ kJ/kmol}
\end{aligned}$$

Substituting,

$$\ln K_p = -(-135{,}556 \text{ kJ/kmol})/[(8.314 \text{ kJ/kmol}\cdot\text{K})(2000 \text{ K})] = 8.152$$

or

$$K_p = \mathbf{3471} \quad (\text{Table A-28}: \ln K_p = 8.145)$$

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16-26E The equilibrium constant of the reaction $H_2 + 1/2O_2 \leftrightarrow H_2O$ is listed in Table A-28 at different temperatures. The data are to be verified at two temperatures using Gibbs function data.

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

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

$H_2 + ½O_2 \leftrightarrow H_2O$

537 R

where

$$\Delta G^*(T) = \nu_{H_2O}\bar{g}^*_{H_2O}(T) - \nu_{H_2}\bar{g}^*_{H_2}(T) - \nu_{O_2}\bar{g}^*_{O_2}(T)$$

At 537 R,

$$\Delta G^*(T) = 1(-98{,}350) - 1(0) - 0.5(0) = -98{,}350 \text{ Btu/lbmol}$$

Substituting,

$$\ln K_p = -(-98{,}350 \text{ Btu/lbmol})/[(1.986 \text{ Btu/lbmol}\cdot\text{R})(537 \text{ R})] = 92.22$$

or

$$K_p = \mathbf{1.12 \times 10^{40}} \quad (\text{Table A-28: } \ln K_p = 92.21)$$

(*b*) At 3240 R,

$$\begin{aligned}
\Delta G^*(T) &= \nu_{H_2O}\bar{g}^*_{H_2O}(T) - \nu_{H_2}\bar{g}^*_{H_2}(T) - \nu_{O_2}\bar{g}^*_{O_2}(T) \\
&= \nu_{H_2O}(\bar{h} - T\bar{s})_{H_2O} - \nu_{H_2}(\bar{h} - T\bar{s})_{H_2} - \nu_{O_2}(\bar{h} - T\bar{s})_{O_2} \\
&= \nu_{H_2O}[(\bar{h}_f + \bar{h}_{3240} - \bar{h}_{537}) - T\bar{s}]_{H_2O} \\
&\quad - \nu_{H_2}[(\bar{h}_f + \bar{h}_{3240} - \bar{h}_{298}) - T\bar{s}]_{H_2} \\
&\quad - \nu_{O_2}[(\bar{h}_f + \bar{h}_{3240} - \bar{h}_{298}) - T\bar{s}]_{O_2} \\
&= 1 \times (-104{,}040 + 31{,}204.5 - 4258 - 3240 \times 61.948) \\
&\quad - 1 \times (0 + 23{,}484.7 - 3640.3 - 3240 \times 44.125) \\
&\quad - 0.5 \times (0 + 25{,}972 - 3725.1 - 3240 \times 63.224) \\
&= -63{,}385 \text{ Btu/lbmol}
\end{aligned}$$

Substituting,

$$\ln K_p = -(-63{,}385 \text{ Btu/lbmol})/[(1.986 \text{ Btu/lbmol.R})(3240 \text{ R})] = 9.85$$

or

$$K_p = \mathbf{1.90 \times 10^{4}} \quad (\text{Table A-28: } \ln K_p = 9.83)$$

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16-27 The equilibrium constant of the reaction CO + 1/2O_2 ↔ CO_2 at 298 K and 2000 K are to be determined, and compared with the values listed in Table A-28.

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

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

$$\mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \Leftrightarrow \mathrm{CO_2}$$
298 K

where

$$\Delta G^*(T) = \nu_{\mathrm{CO2}}\bar{g}^*_{\mathrm{CO2}}(T) - \nu_{\mathrm{CO}}\bar{g}^*_{\mathrm{CO}}(T) - \nu_{\mathrm{O2}}\bar{g}^*_{\mathrm{O2}}(T)$$

At 298 K,

$$\Delta G^*(T) = 1(-394{,}360) - 1(-137{,}150) - 0.5(0) = -257{,}210 \text{ kJ/kmol}$$

where the Gibbs functions are obtained from Table A-26. Substituting,

$$\ln K_p = -\frac{(-257{,}210 \text{ kJ/kmol})}{(8.314 \text{ kJ/kmol}\cdot\text{K})(298 \text{ K})} = \mathbf{103.81}$$

From Table A-28: $\ln K_p = \mathbf{103.76}$

(*b*) At 2000 K,

$$\begin{aligned}\Delta G^*(T) &= \nu_{\mathrm{CO2}}\bar{g}^*_{\mathrm{CO2}}(T) - \nu_{\mathrm{CO}}\bar{g}^*_{\mathrm{CO}}(T) - \nu_{\mathrm{O2}}\bar{g}^*_{\mathrm{O2}}(T)\\ &= \nu_{\mathrm{CO2}}(\bar{h} - T\bar{s})_{\mathrm{CO2}} - \nu_{\mathrm{CO}}(\bar{h} - T\bar{s})_{\mathrm{CO}} - \nu_{\mathrm{O2}}(\bar{h} - T\bar{s})_{\mathrm{O2}}\\ &= 1[(-302{,}128) - (2000)(309.00)] - 1[(-53{,}826) - (2000)(258.48)] - 0.5[(59{,}193) - (2000)(268.53)]\\ &= -110{,}409 \text{ kJ/kmol}\end{aligned}$$

The enthalpies at 2000 K and entropies at 2000 K and 101.3 kPa (1 atm) are obtained from EES. Substituting,

$$\ln K_p = -\frac{(-110{,}409 \text{ kJ/kmol})}{(8.314 \text{ kJ/kmol}\cdot\text{K})(2000 \text{ K})} = \mathbf{6.64}$$

From Table A-28:

$$\ln K_p = \mathbf{6.635}$$

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16-28 EES The effect of varying the percent excess air during the steady-flow combustion of hydrogen is to be studied.

Analysis The combustion equation of hydrogen with stoichiometric amount of air is

$$H_2 + 0.5[O_2 + 3.76N_2] \longrightarrow H_2O + 0.5(3.76)\, N_2$$

For the incomplete combustion with 100% excess air, the combustion equation is

$$H_2 + (1+Ex)(0.5)[O_2 + 3.76N_2] \longrightarrow 0.97\, H_2O + a\, H_2 + b\, O_2 + c\, N_2$$

The coefficients are to be determined from the mass balances

Hydrogen balance: $2 = 0.97 \times 2 + a \times 2 \longrightarrow a = 0.03$

Oxygen balance: $(1+Ex) \times 0.5 \times 2 = 0.97 + b \times 2$

Nitrogen balance: $(1+Ex) \times 0.5 \times 3.76 \times 2 = c \times 2$

Solving the above equations, we find the coefficients (Ex = 1, a = 0.03 b = 0.515, c = 3.76) and write the balanced reaction equation as

$$H_2 + [O_2 + 3.76N_2] \longrightarrow 0.97\, H_2O + 0.03\, H_2 + 0.515\, O_2 + 3.76\, N_2$$

Total moles of products at equilibrium are

$$N_{\text{tot}} = 0.97 + 0.03 + 0.515 + 3.76 = 5.275$$

The assumed equilibrium reaction is

$$H_2O \longleftrightarrow H_2 + 0.5O_2$$

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

$$\Delta G^*(T) = \nu_{H2}\bar{g}^*_{H2}(T_{\text{prod}}) + \nu_{O2}\bar{g}^*_{O2}(T_{\text{prod}}) - \nu_{H2O}\bar{g}^*_{H2O}(T_{\text{prod}})$$

and the Gibbs functions are defined as

$$\bar{g}^*_{H2}(T_{\text{prod}}) = (\bar{h} - T_{\text{prod}}\bar{s})_{H2}$$

$$\bar{g}^*_{O2}(T_{\text{prod}}) = (\bar{h} - T_{\text{prod}}\bar{s})_{O2}$$

$$\bar{g}^*_{H2O}(T_{\text{prod}}) = (\bar{h} - T_{\text{prod}}\bar{s})_{H2O}$$

The equilibrium constant is also given by

$$K_p = \left(\frac{P}{N_{tot}}\right)^{1+0.5-1} \frac{ab^{0.5}}{0.97^1} = \left(\frac{1}{5.275}\right)^{0.5} \frac{(0.03)(0.515)^{0.5}}{0.97} = 0.009664$$

and $\ln K_p = \ln(0.009664) = -4.647$

The corresponding temperature is obtained solving the above equations using EES to be

$$T_{\text{prod}} = \mathbf{2600\ K}$$

This is the temperature at which 97 percent of H_2 will burn into H_2O. The copy of EES solution is given next.

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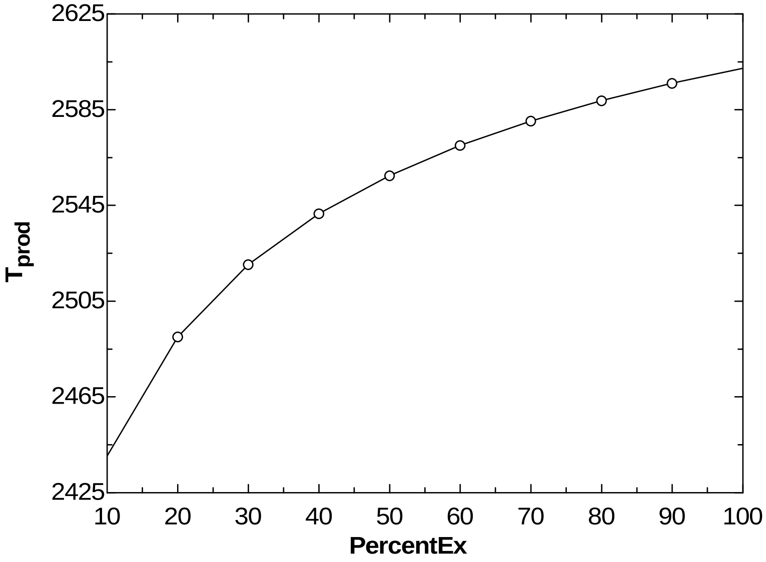
```
"Input Data from parametric table:"
{PercentEx = 10}
Ex = PercentEx/100  "EX = % Excess air/100"
P_prod =101.3"[kPa]"
R_u=8.314 "[kJ/kmol-K]"
"The combustion equation of H2 with stoichiometric amount of air is
H2 + 0.5(O2 + 3.76N2)=H2O +0.5(3.76)N2"
"For the incomplete combustion with 100% excess air, the combustion equation is
H2 + (1+EX)(0.5)(O2 + 3.76N2)=0.97 H2O +aH2 + bO2+cN2"
"Specie balance equations give the values of a, b, and c."
"H, hydrogen"
2 = 0.97*2 + a*2
"O, oxygen"
(1+Ex)*0.5*2=0.97 + b*2
"N, nitrogen"
(1+Ex)*0.5*3.76 *2 = c*2
N_tot =0.97+a +b +c  "Total kilomoles of products at equilibrium"
"The assumed equilibrium reaction is
H2O=H2+0.5O2"
"The following equations provide the specific Gibbs function (g=h-Ts) for
each H2mponent in the product gases as a function of its temperature, T_prod,
at 1 atm pressure, 101.3 kPa"
g_H2O=Enthalpy(H2O,T=T_prod )-T_prod *Entropy(H2O,T=T_prod ,P=101.3)
g_H2=Enthalpy(H2,T=T_prod )-T_prod *Entropy(H2,T=T_prod ,P=101.3)
g_O2=Enthalpy(O2,T=T_prod )-T_prod *Entropy(O2,T=T_prod ,P=101.3)
"The standard-state Gibbs function is"
DELTAG =1*g_H2+0.5*g_O2-1*g_H2O
"The equilibrium constant is given by Eq. 15-14."
K_P  = exp(-DELTAG /(R_u*T_prod ))
P=P_prod /101.3"atm"
"The equilibrium constant is also given by Eq. 15-15."
"K_ P = (P/N_tot)^(1+0.5-1)*(a^1*b^0.5)/(0.97^1)"
sqrt(P/N_tot )*a *sqrt(b )=K_P *0.97
lnK_p = ln(k_P)
```

ln K_p	PercentEx [%]	T_{prod} [K]
-5.414	10	2440
-5.165	20	2490
-5.019	30	2520
-4.918	40	2542
-4.844	50	2557
-4.786	60	2570
-4.739	70	2580
-4.7	80	2589
-4.667	90	2596
-4.639	100	2602



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16-29 The equilibrium constant of the reaction $CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$ at 25°C is to be determined.

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

$$K_p = e^{-\Delta G^*(T)/R_uT} \quad \text{or} \quad \ln K_p = -\Delta G^*(T)/R_uT$$

where

$$\Delta G^*(T) = \nu_{CO_2}\overline{g}^*_{CO_2}(T) + \nu_{H_2O}\overline{g}^*_{H_2O}(T) - \nu_{CH_4}\overline{g}^*_{CH_4}(T) - \nu_{O_2}\overline{g}^*_{O_2}(T)$$

$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$

25°C

At 25°C,

$$\Delta G^*(T) = 1(-394{,}360) + 2(-228{,}590) - 1(-50{,}790) - 2(0) = -800{,}750 \text{ kJ / kmol}$$

Substituting,

$$\ln K_p = -(-800{,}750 \text{ kJ/kmol})/[(8.314 \text{ kJ/kmol}\cdot\text{K})(298 \text{ K})] = 323.04$$

or

$$K_p = \mathbf{1.96 \times 10^{140}}$$

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16-30 The equilibrium constant of the reaction $CO_2 \leftrightarrow CO + 1/2O_2$ is listed in Table A-28 at different temperatures. It is to be verified using Gibbs function data.

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

$CO_2 \leftrightarrow CO + ½O_2$
298 K

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

where $\Delta G^*(T) = \nu_{CO}\bar{g}^*_{CO}(T) + \nu_{O_2}\bar{g}^*_{O_2}(T) - \nu_{CO_2}\bar{g}^*_{CO_2}(T)$

At 298 K,

$$\Delta G^*(T) = 1(-137{,}150) + 0.5(0) - 1(-394{,}360) = 257{,}210 \text{ kJ/kmol}$$

Substituting,

$$\ln K_p = -(257{,}210 \text{ kJ/kmol})/[(8.314 \text{ kJ/kmol}\cdot\text{K})(298 \text{ K})] = -103.81$$

or $\quad K_p = \mathbf{8.24\times10^{-46}} \quad (\text{Table A-28}: \ln K_p = -103.76)$

(*b*) At 1800 K,

$$\begin{aligned}
\Delta G^*(T) &= \nu_{CO}\bar{g}^*_{CO}(T) + \nu_{O_2}\bar{g}^*_{O_2}(T) - \nu_{CO_2}\bar{g}^*_{CO_2}(T) \\
&= \nu_{CO}(\bar{h} - T\bar{s})_{CO} + \nu_{O_2}(\bar{h} - T\bar{s})_{O_2} - \nu_{CO_2}(\bar{h} - T\bar{s})_{CO_2} \\
&= \nu_{CO}[(\bar{h}_f + \bar{h}_{1800} - \bar{h}_{298}) - T\bar{s}]_{CO} \\
&\quad + \nu_{O_2}[(\bar{h}_f + \bar{h}_{1800} - \bar{h}_{298}) - T\bar{s}]_{O_2} \\
&\quad - \nu_{CO_2}[(\bar{h}_f + \bar{h}_{1800} - \bar{h}_{298}) - T\bar{s}]_{CO_2} \\
&= 1\times(-110{,}530 + 58{,}191 - 8669 - 1800\times254.797) \\
&\quad + 0.5\times(0 + 60{,}371 - 8682 - 1800\times264.701) \\
&\quad - 1\times(-393{,}520 + 88{,}806 - 9364 - 1800\times302.884) \\
&= 127{,}240.2 \text{ kJ/kmol}
\end{aligned}$$

Substituting, $\quad \ln K_p = -(127{,}240.2 \text{ kJ/kmol})/[(8.314 \text{ kJ/kmol}\cdot\text{K})(1800 \text{ K})] = -8.502$

or $\quad K_p = \mathbf{2.03\times10^{-4}} \quad (\text{Table A-28}: \ln K_p = -8.497)$

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16-31 [*Also solved by EES on enclosed CD***]** Carbon monoxide is burned with 100 percent excess air. The temperature at which 97 percent of CO burn to CO_2 is to be determined.

Assumptions **1** The equilibrium composition consists of CO_2, CO, O_2, and N_2. **2** The constituents of the mixture are ideal gases.

Analysis Assuming N_2 to remain as an inert gas, the stoichiometric and actual reactions can be written as

Stoichiometric: $\mathrm{CO}+\frac{1}{2}\mathrm{O}_2 \Leftrightarrow \mathrm{CO}_2$ (thus $\nu_{\mathrm{CO}_2}=1,\ \nu_{\mathrm{CO}}=1,\ \text{and}\ \nu_{\mathrm{O}_2}=\frac{1}{2}$)

Actual: $\mathrm{CO}+1(\mathrm{O}_2+3.76\,\mathrm{N}_2) \longrightarrow \underbrace{0.97\,\mathrm{CO}_2}_{\text{product}}+\underbrace{0.03\,\mathrm{CO}+0.515\,\mathrm{O}_2}_{\text{reactants}}+\underbrace{3.76\,\mathrm{N}_2}_{\text{inert}}$

The equilibrium constant K_p can be determined from

$$K_p=\frac{N_{\mathrm{CO}_2}^{\nu_{\mathrm{CO}_2}}}{N_{\mathrm{CO}}^{\nu_{\mathrm{CO}}}N_{\mathrm{O}_2}^{\nu_{\mathrm{O}_2}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{\mathrm{CO}_2}-\nu_{\mathrm{CO}}-\nu_{\mathrm{O}_2})}$$

$$=\frac{0.97}{0.03\times 0.515^{0.5}}\left(\frac{1}{0.97+0.03+0.515+3.76}\right)^{1-1.5}$$

$$=103.48$$

CO + ½O_2 ↔ CO_2
97 %
1 atm

From Table A-28, the temperature corresponding to this K_p value is T = **2276 K**

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16-32 EES Problem 16-31 is reconsidered. The effect of varying the percent excess air during the steady-flow process from 0 to 200 percent on the temperature at which 97 percent of CO burn into CO2 is to be studied.

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

```
"To solve this problem, we need to give EES a guess value for T_prop other than
the default value of 1.  Set the guess value of T_prod to 1000 K by selecting  Variable
Infromation in the Options menu.  Then press F2 or click the Calculator icon."

"Input Data from the diagram window:"
{PercentEx = 100}
Ex = PercentEx/100  "EX = % Excess air/100"
P_prod =101.3 [kPa]
R_u=8.314 [kJ/kmol-K]

"The combustion equation of CO with stoichiometric amount of air is
CO + 0.5(O2 + 3.76N2)=CO2 +0.5(3.76)N2"

"For the incomplete combustion with 100% excess air, the combustion equation is
CO + (!+EX)(0.5)(O2 + 3.76N2)=0.97 CO2 +aCO + bO2+cN2"

"Specie balance equations give the values of a, b, and c."
"C, Carbon"
1 = 0.97 + a
"O, oxygen"
1 +(1+Ex)*0.5*2=0.97*2 + a *1 + b*2
"N, nitrogen"
(1+Ex)*0.5*3.76 *2 = c*2
N_tot =0.97+a +b +c  "Total kilomoles of products at equilibrium"

"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=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)

"The standard-state Gibbs function is"
DELTAG =1*g_CO+0.5*g_O2-1*g_CO2

"The equilibrium constant is given by Eq. 15-14."
K_P  = exp(-DELTAG /(R_u*T_prod ))
P=P_prod /101.3"atm"
"The equilibrium constant is also given by Eq. 15-15."
"K_ P = (P/N_tot)^(1+0.5-1)*(a^1*b^0.5)/(0.97^1)"

sqrt(P/N_tot )*a *sqrt(b )=K_P *0.97
lnK_p = ln(k_P)

"Compare the value of lnK_p calculated by EES with the value of
lnK_p from table A-28 in the text."
```

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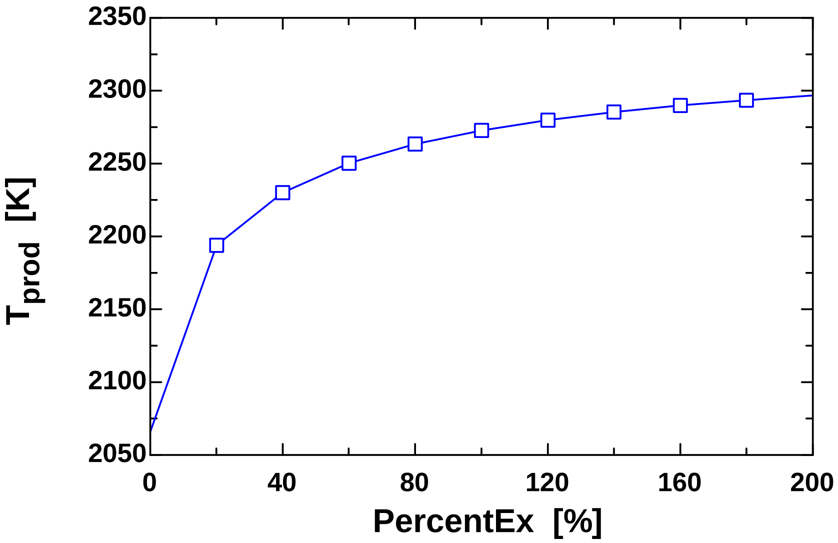
PercentEx [%]	T_{prod} [K]
0	2066
20	2194
40	2230
60	2250
80	2263
100	2273
120	2280
140	2285
160	2290
180	2294
200	2297



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16-33E Carbon monoxide is burned with 100 percent excess air. The temperature at which 97 percent of CO burn to CO_2 is to be determined.

Assumptions **1** The equilibrium composition consists of CO_2, CO, O_2, and N_2. **2** The constituents of the mixture are ideal gases.

Analysis Assuming N_2 to remain as an inert gas, the stoichiometric and actual reactions can be written as

Stoichiometric: $CO + \tfrac{1}{2}O_2 \Leftrightarrow CO_2$ (thus $\nu_{CO_2} = 1,\ \nu_{CO} = 1,\ \text{and}\ \nu_{O_2} = \tfrac{1}{2}$)

Actual: $CO + 1(O_2 + 3.76N_2) \longrightarrow \underbrace{0.97CO_2}_{\text{product}} + \underbrace{0.03CO + 0.515O_2}_{\text{reactants}} + \underbrace{3.76N_2}_{\text{inert}}$

The equilibrium constant K_p can be determined from

$$
\begin{aligned}
K_p &= \frac{N_{CO_2}^{\nu_{CO_2}}}{N_{CO}^{\nu_{CO}} N_{O_2}^{\nu_{O_2}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{CO_2}-\nu_{CO}-\nu_{O_2})} \\
&= \frac{0.97}{0.03 \times 0.515^{0.5}}\left(\frac{1}{0.97+0.03+0.515+3.76}\right)^{1-1.5} \\
&= 103.48
\end{aligned}
$$

CO + ½O_2 ↔ CO_2
97 %
1 atm

From Table A-28, the temperature corresponding to this K_p value is T = **2276 K** = **4097 R**

16-34 Hydrogen is burned with 150 percent theoretical air. The temperature at which 98 percent of H_2 will burn to H_2O is to be determined.

Assumptions **1** The equilibrium composition consists of H_2O, H_2, O_2, and N_2. **2** The constituents of the mixture are ideal gases.

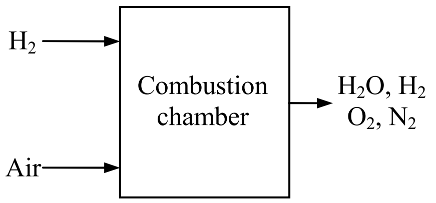
Analysis Assuming N_2 to remain as an inert gas, the stoichiometric and actual reactions can be written as

Stoichiometric: $H_2 + \tfrac{1}{2}O_2 \Leftrightarrow H_2O$ (thus $\nu_{H_2O} = 1, \nu_{H_2} = 1,\ \text{and}\ \nu_{O_2} = \tfrac{1}{2}$)

Actual: $H_2 + 0.75(O_2 + 3.76N_2) \longrightarrow \underbrace{0.98H_2O}_{\text{product}} + \underbrace{0.02H_2 + 0.26O_2}_{\text{reactants}} + \underbrace{2.82N_2}_{\text{inert}}$

The equilibrium constant K_p can be determined from

$$
\begin{aligned}
K_p &= \frac{N_{H_2O}^{\nu_{H_2O}}}{N_{H_2}^{\nu_{H_2}} N_{O_2}^{\nu_{O_2}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{H_2O}-\nu_{H_2}-\nu_{O_2})} \\
&= \frac{0.98}{0.02 \times 0.26^{0.5}}\left(\frac{1}{0.98+0.02+0.26+2.82}\right)^{1-1.5} \\
&= 194.11
\end{aligned}
$$



From Table A-28, the temperature corresponding to this K_p value is T = **2472 K**.

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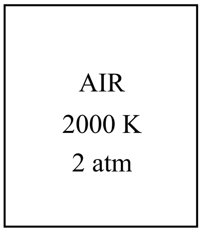
16-35 Air is heated to a high temperature. The equilibrium composition at that temperature is to be determined.

Assumptions **1** The equilibrium composition consists of N_2, O_2, and NO. **2** The constituents of the mixture are ideal gases.

Analysis The stoichiometric and actual reactions in this case are



Stoichiometric: $\frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2 \Leftrightarrow \text{NO}$ (thus $\nu_{\text{NO}} = 1,\ \nu_{\text{N}_2} = \frac{1}{2}$, and $\nu_{\text{O}_2} = \frac{1}{2}$)

Actual: $3.76\,\text{N}_2 + \text{O}_2 \longrightarrow \underbrace{x\,\text{NO}}_{\text{prod.}} + \underbrace{y\,\text{N}_2 + z\,\text{O}_2}_{\text{reactants}}$

N balance: $7.52 = x + 2y$ or $y = 3.76 - 0.5x$

O balance: $2 = x + 2z$ or $z = 1 - 0.5x$

Total number of moles: $N_{\text{total}} = x + y + z = x + 4.76 - x = 4.76$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{\text{NO}}^{\nu_{\text{NO}}}}{N_{\text{N}_2}^{\nu_{\text{N}_2}} N_{\text{O}_2}^{\nu_{\text{O}_2}}} \left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{\text{NO}} - \nu_{\text{N}_2} - \nu_{\text{O}_2})}$$

From Table A-28, ln K_p = -3.931 at 2000 K. Thus K_p = 0.01962. Substituting,

$$0.01962 = \frac{x}{(3.76 - 0.5x)^{0.5}(1 - 0.5x)^{0.5}} \left(\frac{2}{4.76}\right)^{1-1}$$

Solving for x,

$$x = 0.0376$$

Then,

$$y = 3.76\text{-}0.5x = 3.7412$$

$$z = 1\text{-}0.5x = 0.9812$$

Therefore, the equilibrium composition of the mixture at 2000 K and 2 atm is

$$0.0376\text{NO} + 3.7412\text{N}_2 + 0.9812\text{O}_2$$

The equilibrium constant for the reactions $\text{O}_2 \Leftrightarrow 2\text{O}$ (ln K_p = -14.622) and $\text{N}_2 \Leftrightarrow 2\text{N}$ (ln K_p = -41.645) are much smaller than that of the specified reaction (ln K_p = -3.931). Therefore, it is realistic to assume that no monatomic oxygen or nitrogen will be present in the equilibrium mixture. Also the equilibrium composition is in this case is independent of pressure since $\Delta\nu = 1 - 0.5 - 0.5 = 0$.

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16-36 Hydrogen is heated to a high temperature at a constant pressure. The percentage of H_2 that will dissociate into H is to be determined.

Assumptions **1** The equilibrium composition consists of H_2 and H. **2** The constituents of the mixture are ideal gases.

Analysis The stoichiometric and actual reactions can be written as

Stoichiometric: $\mathrm{H_2} \Leftrightarrow 2\mathrm{H}$ (thus $\nu_{\mathrm{H_2}} = 1$ and $\nu_{\mathrm{H}} = 2$)

Actual: $\mathrm{H_2} \longrightarrow \underbrace{x\mathrm{H_2}}_{\text{react.}} + \underbrace{y\mathrm{H}}_{\text{prod.}}$

H_2
3200 K
8 atm

H balance: $2 = 2x + y$ or $y = 2 - 2x$

Total number of moles: $N_{\text{total}} = x + y = x + 2 - 2x = 2 - x$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{\mathrm{H}}^{\nu_{\mathrm{H}}}}{N_{\mathrm{H_2}}^{\nu_{\mathrm{H_2}}}} \left(\frac{P}{N_{\text{total}}} \right)^{\nu_{\mathrm{H}} - \nu_{\mathrm{H_2}}}$$

From Table A-28, ln $K_p = -2.534$ at 3200 K. Thus $K_p = 0.07934$. Substituting,

$$0.07934 = \frac{(2-2x)^2}{x} \left(\frac{8}{2-x} \right)^{2-1}$$

Solving for x, $x = 0.95$

Thus the percentage of H_2 which dissociates to H at 3200 K and 8 atm is

$1 - 0.95 = 0.05$ or **5.0%**

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16-37E A mixture of CO, O_2, and N_2 is heated to a high temperature at a constant pressure. The equilibrium composition is to be determined.

Assumptions **1** The equilibrium composition consists of CO_2, CO, O_2, and N_2. **2** The constituents of the mixture are ideal gases.

Analysis The stoichiometric and actual reactions in this case are

2 CO
2 O_2
6 N_2
4320 R
3 atm

Stoichiometric: $CO+\frac{1}{2}O_2 \Leftrightarrow CO_2 \quad (\text{thus } \nu_{CO_2}=1, \nu_{CO}=1, \text{ and } \nu_{O_2}=\frac{1}{2})$

Actual: $2\,CO+2\,O_2+6\,N_2 \longrightarrow \underbrace{x\,CO_2}_{\text{products}}+\underbrace{y\,CO+z\,O_2}_{\text{reactants}}+\underset{\text{inert}}{6\,N_2}$

C balance: $2=x+y \longrightarrow y=2-x$

O balance: $6=2x+y+2z \longrightarrow z=2-0.5x$

Total number of moles: $N_{\text{total}}=x+y+z+6=10-0.5x$

The equilibrium constant relation can be expressed as

$$K_p=\frac{N_{CO_2}^{\nu_{CO_2}}}{N_{CO}^{\nu_{CO}}N_{O_2}^{\nu_{O_2}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{CO_2}-\nu_{CO}-\nu_{O_2})}$$

From Table A-28, $\ln K_p=3.860$ at $T=4320\text{ R}=2400\text{ K}$. Thus $K_p=47.465$. Substituting,

$$47.465=\frac{x}{(2-x)(2-0.5x)^{0.5}}\left(\frac{3}{10-0.5x}\right)^{1-1.5}$$

Solving for x,

$$x=1.930$$

Then,

$$y=2-x=0.070$$

$$z=2-0.5x=1.035$$

Therefore, the equilibrium composition of the mixture at 2400 K and 3 atm is

$$\mathbf{1.930CO_2+0.070CO+1.035O_2+6N_2}$$

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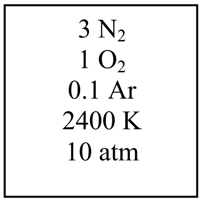
16-38 A mixture of N_2, O_2, and Ar is heated to a high temperature at a constant pressure. The equilibrium composition is to be determined.

Assumptions **1** The equilibrium composition consists of N_2, O_2, Ar, and NO. **2** The constituents of the mixture are ideal gases.

Analysis The stoichiometric and actual reactions in this case are



Stoichiometric: $\frac{1}{2}N_2 + \frac{1}{2}O_2 \Leftrightarrow NO$ (thus $\nu_{NO} = 1,\ \nu_{N_2} = \frac{1}{2}$, and $\nu_{O_2} = \frac{1}{2}$)

Actual: $3N_2 + O_2 + 0.1\,Ar \longrightarrow \underbrace{x\,NO}_{\text{prod.}} + \underbrace{y\,N_2 + z\,O_2}_{\text{reactants}} + \underbrace{0.1\,Ar}_{\text{inert}}$

N balance: $6 = x + 2y \longrightarrow y = 3 - 0.5x$

O balance: $2 = x + 2z \longrightarrow z = 1 - 0.5x$

Total number of moles: $N_{total} = x + y + z + 0.1 = 4.1$

The equilibrium constant relation becomes,

$$K_p = \frac{N_{NO}^{\nu_{NO}}}{N_{N_2}^{\nu_{N_2}} N_{O_2}^{\nu_{O_2}}}\left(\frac{P}{N_{total}}\right)^{(\nu_{NO}-\nu_{N_2}-\nu_{O_2})} = \frac{x}{y^{0.5}z^{0.5}}\left(\frac{P}{N_{total}}\right)^{1-0.5-0.5}$$

From Table A-28, $\ln K_p = -3.019$ at 2400 K. Thus $K_p = 0.04885$. Substituting,

$$0.04885 = \frac{x}{(3-0.5x)^{0.5}(1-0.5x)^{0.5}} \times 1$$

Solving for x,

$x = 0.0823$

Then,

$y = 3 - 0.5x = 2.9589$

$z = 1 - 0.5x = 0.9589$

Therefore, the equilibrium composition of the mixture at 2400 K and 10 atm is

$$\mathbf{0.0823NO + 2.9589N_2 + 0.9589O_2 + 0.1Ar}$$

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16-39 The mole fraction of sodium that ionizes according to the reaction Na ⇔ $Na^+ + e^-$ at 2000 K and 0.8 atm is to be determined.

Assumptions All components behave as ideal gases.

Analysis The stoichiometric and actual reactions can be written as

Na ⇔ $Na^+ + e^-$
2000 K
0.8 atm

Stoichiometric: $Na \Leftrightarrow Na^+ + e^-$ (thus $\nu_{Na} = 1,\ \nu_{Na^+} = 1$ and $\nu_{e^-} = 1$)

Actual: $$Na \longrightarrow \underbrace{xNa}_{\text{react.}} + \underbrace{yNa^+ + ye^-}_{\text{products}}$$

Na balance: $1 = x + y \quad or \quad y = 1 - x$

Total number of moles: $N_{total} = x + 2y = 2 - x$

The equilibrium constant relation becomes,

$$K_p = \frac{N_{Na}^{\nu_{Na}} N_{e^-}^{\nu_{e^-}}}{N_{Na}^{\nu_{Na}}}\left(\frac{P}{N_{total}}\right)^{(\nu_{Na^+} + \nu_{e^-} - \nu_{Na})} = \frac{y^2}{x}\left(\frac{P}{N_{total}}\right)^{1+1-1}$$

Substituting,

$$0.668 = \frac{(1-x)^2}{x}\left(\frac{0.8}{2-x}\right)$$

Solving for x,

$x = 0.325$

Thus the fraction of Na which dissociates into Na^+ and e^- is

1 - 0.325 = 0.675 or **67.5%**

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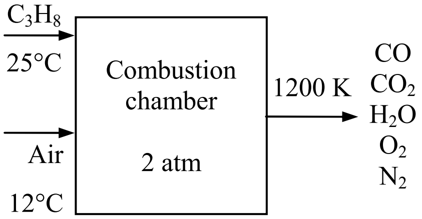
16-40 Liquid propane enters a combustion chamber. The equilibrium composition of product gases and the rate of heat transfer from the combustion chamber are to be determined.

Assumptions **1** The equilibrium composition consists of CO_2, H_2O, CO, N_2, and O_2. **2** The constituents of the mixture are ideal gases.



Analysis (*a*) Considering 1 kmol of C_3H_8, the stoichiometric combustion equation can be written as

$$C_3H_8(\ell) + a_{\text{th}}(O_2 + 3.76N_2) \longrightarrow 3CO_2 + 4H_2O + 3.76a_{\text{th}}N_2$$

where a_{th} is the stoichiometric coefficient and is determined from the O_2 balance,

$$2.5a_{\text{th}} = 3 + 2 + 1.5a_{\text{th}} \longrightarrow a_{\text{th}} = 5$$

Then the actual combustion equation with 150% excess air and some CO in the products can be written as

$$C_3H_8(\ell) + 12.5(O_2 + 3.76N_2) \longrightarrow xCO_2 + (3-x)CO + (9-0.5x)O_2 + 4H_2O + 47N_2$$

After combustion, there will be no C_3H_8 present in the combustion chamber, and H_2O will act like an inert gas. The equilibrium equation among CO_2, CO, and O_2 can be expressed as

$$CO_2 \Leftrightarrow CO + \tfrac{1}{2}O_2 \quad (\text{thus } \nu_{CO_2} = 1,\ \nu_{CO} = 1,\ \text{and } \nu_{O_2} = \tfrac{1}{2})$$

and

$$K_p = \frac{N_{CO}^{\nu_{CO}} N_{O_2}^{\nu_{O_2}}}{N_{CO_2}^{\nu_{CO_2}}} \left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{CO}+\nu_{O_2}-\nu_{CO_2})}$$

where

$$N_{\text{total}} = x + (3-x) + (9-0.5x) + 4 + 47 = 63 - 0.5x$$

From Table A-28, $\ln K_p = -17.871$ at 1200 K. Thus $K_p = 1.73\times10^{-8}$. Substituting,

$$1.73\times10^{-8} = \frac{(3-x)(9-0.5x)^{0.5}}{x}\left(\frac{2}{63-0.5x}\right)^{1.5-1}$$

Solving for x,

$$x = 2.9999999 \cong 3.0$$

Therefore, the amount CO in the product gases is negligible, and it can be disregarded with no loss in accuracy. Then the combustion equation and the equilibrium composition can be expressed as

$$C_3H_8(\ell) + 12.5(O_2 + 3.76N_2) \longrightarrow 3CO_2 + 7.5O_2 + 4H_2O + 47N_2$$

and

$$\mathbf{3CO_2 + 7.5O_2 + 4H_2O + 47N_2}$$

(*b*) The heat transfer for this combustion process is determined from the steady-flow energy balance $E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$ on the combustion chamber with $W = 0$,

$$-Q_{\text{out}} = \sum N_P\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_P - \sum N_R\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_R$$

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Assuming the air and the combustion products to be ideal gases, we have $h = h(T)$. From the tables, (The $\bar{h}_f^\circ$ of liquid propane is obtained by adding the h_{fg} at 25°C to $\bar{h}_f^\circ$ of gaseous propane).

Substance	$\bar{h}_f^\circ$ kJ/kmol	$\bar{h}_{285\ K}$ kJ/kmol	$\bar{h}_{298\ K}$ kJ/kmol	$\bar{h}_{1200\ K}$ kJ/kmol
C_3H_8 (ℓ)	-118,910	---	---	---
O_2	0	8696.5	8682	38,447
N_2	0	8286.5	8669	36,777
H_2O (*g*)	-241,820	---	9904	44,380
CO_2	-393,520	---	9364	53,848

Substituting,

$$\begin{aligned}-Q_{\text{out}} &= 3(-393{,}520+53{,}848-9364)+4(-241{,}820+44{,}380-9904)\\ &\quad +7.5(0+38{,}447-8682)+47(0+36{,}777-8669)\\ &\quad -1(-118{,}910+h_{298}-h_{298})-12.5(0+8296.5-8682)\\ &\quad -47(0+8186.5-8669)\\ &= -185{,}764 \text{ kJ / kmol of } C_3H_8\end{aligned}$$

or

$$Q_{\text{out}} = 185{,}764 \text{ kJ / kmol of } C_3H_8$$

The mass flow rate of C_3H_8 can be expressed in terms of the mole numbers as

$$\dot{N} = \frac{\dot{m}}{M} = \frac{1.2 \text{ kg / min}}{44 \text{ kg / kmol}} = 0.02727 \text{ kmol / min}$$

Thus the rate of heat transfer is

$$\dot{Q}_{\text{out}} = \dot{N} \times Q_{\text{out}} = (0.02727 \text{ kmol/min})(185{,}746 \text{ kJ/kmol}) = \mathbf{5066\ kJ/min}$$

The equilibrium constant for the reaction $\frac{1}{2}N_2 + \frac{1}{2}O_2 \Leftrightarrow NO$ is $\ln K_p$ = -7.569, which is very small. This indicates that the amount of NO formed during this process will be very small, and can be disregarded.

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16-41 EES Problem 16-40 is reconsidered. It is to be investigated if it is realistic to disregard the presence of NO in the product gases.

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

```
"To solve this problem,  the Gibbs function of the product gases is minimized. Click on the
Min/Max icon."

For this problem at 1200 K the moles of  CO are 0.000 and moles of NO are 0.000, thus we
can disregard both the CO and NO.  However, try some product temperatures above 1286 K
and observe the sign change on the Q_out and the amout of CO and NO present as the
product temperature increases."

"The reaction of C3H8(liq) with excess air can be written:

   C3H8(l) + (1+Ex)A_th (O2+3.76N2) = a C02 + b CO + c H2O + d N2 + e O2 + f NO

The coefficients A_th and EX are the theoretical oxygen and the percent excess air on a decimal
basis.   Coefficients a, b, c, d, e, and f are found by minimiming the Gibbs Free Energy at a total
pressure of the product gases P_Prod and the product  temperature T_Prod.

The equilibrium solution can be found by applying the Law of Mass Action or by minimizing the
Gibbs function.  In this problem, the Gibbs function is directly minimized using the optimization
capabilities built into EES.

To run this program, click on the Min/Max icon.  There are six compounds present  in the products
subject to four specie balances, so there are two degrees of freedom.   Minimize the Gibbs
function of the product gases with respect to two molar quantities such as coefficients b and f.
The equilibrium mole numbers a, b, c, d, e, and f  will be determined and displayed in the Solution
window."

PercentEx = 150 [%]
Ex = PercentEx/100  "EX = % Excess air/100"
P_prod =2*P_atm
T_Prod=1200 [K]
m_dot_fuel = 0.5 [kg/s]
Fuel$='C3H8'
T_air = 12+273 "[K]"
T_fuel = 25+273 "[K]"
P_atm = 101.325 [kPa]
R_u=8.314 [kJ/kmol-K]

"Theoretical combustion of C3H8 with oxygen:
C3H8 + A_th O2 = 3 C02 + 4 H2O "
2*A_th = 3*2 + 4*1

"Balance the reaction for 1 kmol of C3H8"
"C3H8(l) + (1+Ex)A_th (O2+3.76N2) = a C02 + b CO + c H2O + d N2 + e O2 + f NO"
b_max = 3
f_max = (1+Ex)*A_th*3.76*2
e_guess=Ex*A_th
1*3 = a*1+b*1 "Carbon balance"
1*8=c*2
"Hydrogen balance"
(1+Ex)*A_th*2=a*2+b*1+c*1+e*2+f*1 "Oxygen balance"
(1+Ex)*A_th*3.76*2=d*2+f*1 "Nitrogen balance"
```

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```
"Total moles and mole fractions"
N_Total=a+b+c+d+e+f
y_CO2=a/N_Total;  y_CO=b/N_Total; y_H2O=c/N_Total; y_N2=d/N_Total; y_O2=e/N_Total;
y_NO=f/N_Total

"The following equations provide the specific Gibbs function for each component as a function of
its molar amount"
g_CO2=Enthalpy(CO2,T=T_Prod)-T_Prod*Entropy(CO2,T=T_Prod,P=P_Prod*y_CO2)
g_CO=Enthalpy(CO,T=T_Prod)-T_Prod*Entropy(CO,T=T_Prod,P=P_Prod*y_CO)
g_H2O=Enthalpy(H2O,T=T_Prod)-T_Prod*Entropy(H2O,T=T_Prod,P=P_Prod*y_H2O)
g_N2=Enthalpy(N2,T=T_Prod)-T_Prod*Entropy(N2,T=T_Prod,P=P_Prod*y_N2)
g_O2=Enthalpy(O2,T=T_Prod)-T_Prod*Entropy(O2,T=T_Prod,P=P_Prod*y_O2)
g_NO=Enthalpy(NO,T=T_Prod)-T_Prod*Entropy(NO,T=T_Prod,P=P_Prod*y_NO)

"The extensive Gibbs function is the sum of the products of the specific Gibbs function and the
molar amount of each substance"
Gibbs=a*g_CO2+b*g_CO+c*g_H2O+d*g_N2+e*g_O2+f*g_NO

"For the energy balance, we adjust the value of the enthalpy of gaseous propane given by EES:"
h_fg_fuel = 15060"[kJ/kmol]" "Table A.27"
h_fuel = enthalpy(Fuel$,T=T_fuel)-h_fg_fuel
"Energy balance for the combustion process:"
"C3H8(l) + (1+Ex)A_th (O2+3.76N2) = a C02 + b CO + c H2O + d N2 + e O2 + f NO"
HR =Q_out+HP
HR=h_fuel+ (1+Ex)*A_th*(enthalpy(O2,T=T_air)+3.76*enthalpy(N2,T=T_air))
HP=a*enthalpy(CO2,T=T_prod)+b*enthalpy(CO,T=T_prod)+c*enthalpy(H2O,T=T_prod)+d*enthal
py(N2,T=T_prod)+e*enthalpy(O2,T=T_prod)+f*enthalpy(NO,T=T_prod)
"The heat transfer rate is:"
Q_dot_out=Q_out/molarmass(Fuel$)*m_dot_fuel "[kW]"
```

SOLUTION

```
a=3.000 [kmol]              g_CO2=-707231 [kJ/kmol]         Q_dot_out=2140 [kW]
A_th=5                      g_H2O=-515974 [kJ/kmol]         Q_out=188732 [kJ/kmol_fuel]
b=0.000 [kmol]              g_N2=-248486 [kJ/kmol]          R_u=8.314 [kJ/kmol-K]
b_max=3                     g_NO=-342270 [kJ/kmol]          T_air=285 [K]
c=4.000 [kmol]              g_O2=-284065 [kJ/kmol]          T_fuel=298 [K]
d=47.000 [kmol]             HP=-330516.747 [kJ/kmol]        T_Prod=1200.00 [K]
e=7.500 [kmol]              HR=-141784.529 [kJ/kmol]        y_CO=1.626E-15
Ex=1.5                      h_fg_fuel=15060 [kJ/kmol]       y_CO2=0.04878
e_guess=7.5                 h_fuel=-118918 [kJ/kmol]        y_H2O=0.06504
f=0.000 [kmol]              m_dot_fuel=0.5 [kg/s]           y_N2=0.7642
Fuel$='C3H8'                N_Total=61.5 [kmol/kmol_fuel]   y_NO=7.857E-08
f_max=94                    PercentEx=150 [%]               y_O2=0.122
Gibbs=-17994897 [kJ]        P_atm=101.3 [kPa]
g_CO=-703496 [kJ/kmol]      P_prod=202.7 [kPa]
```

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16-42 Oxygen is heated during a steady-flow process. The rate of heat supply needed during this process is to be determined for two cases.

Assumptions **1** The equilibrium composition consists of O_2 and O. **2** All components behave as ideal gases.

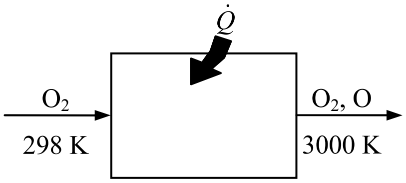
Analysis (*a*) Assuming some O_2 dissociates into O, the dissociation equation can be written as

$$O_2 \longrightarrow x\,O_2 + 2(1-x)O$$

The equilibrium equation among O_2 and O can be expressed as

$$O_2 \Leftrightarrow 2O \quad (\text{thus } \nu_{O_2} = 1 \text{ and } \nu_O = 2)$$

Assuming ideal gas behavior for all components, the equilibrium constant relation can be expressed as



$$K_p = \frac{N_O^{\nu_O}}{N_{O_2}^{\nu_{O_2}}}\left(\frac{P}{N_{\text{total}}}\right)^{\nu_O-\nu_{O_2}}$$

where $N_{\text{total}} = x + 2(1-x) = 2 - x$

From Table A-28, $\ln K_p = -4.357$ at 3000 K. Thus $K_p = 0.01282$. Substituting,

$$0.01282 = \frac{(2-2x)^2}{x}\left(\frac{1}{2-x}\right)^{2-1}$$

Solving for x gives $x = 0.943$

Then the dissociation equation becomes

$$O_2 \longrightarrow 0.943\,O_2 + 0.114\,O$$

The heat transfer for this combustion process is determined from the steady-flow energy balance $E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$ on the combustion chamber with $W = 0$,

$$Q_{\text{in}} = \sum N_P\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_P - \sum N_R\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_R$$

Assuming the O_2 and O to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\bar{h}_f^\circ$ **kJ/kmol**	$\bar{h}_{298\text{ K}}$ **kJ/kmol**	$\bar{h}_{3000\text{ K}}$ **kJ/kmol**
O	249,190	6852	63,425
O_2	0	8682	106,780

Substituting,

$$Q_{\text{in}} = 0.943(0 + 106{,}780 - 8682) + 0.114(249{,}190 + 63{,}425 - 6852) - 0 = 127{,}363 \text{ kJ / kmol } O_2$$

The mass flow rate of O_2 can be expressed in terms of the mole numbers as

$$\dot{N} = \frac{\dot{m}}{M} = \frac{0.5 \text{ kg/min}}{32 \text{ kg/kmol}} = 0.01563 \text{ kmol/min}$$

Thus the rate of heat transfer is

$$\dot{Q}_{\text{in}} = \dot{N} \times Q_{\text{in}} = (0.01563 \text{ kmol/min})(127{,}363 \text{ kJ/kmol}) = \mathbf{1990 \text{ kJ/min}}$$

(*b*) If no O_2 dissociates into O, then the process involves no chemical reactions and the heat transfer can be determined from the steady-flow energy balance for nonreacting systems to be

$$\dot{Q}_{\text{in}} = \dot{m}(h_2 - h_1) = \dot{N}(\bar{h}_2 - \bar{h}_1) = (0.01563 \text{ kmol/min})(106{,}780 - 8682) \text{ kJ/kmol} = \mathbf{1533 \text{ kJ/min}}$$

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16-43 The equilibrium constant, K_p is to be estimated at 2500 K for the reaction CO + H2O = CO2 + H2.

Analysis (*a*) 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

$$\Delta G^*(T) = \nu_{\text{CO2}}\bar{g}^*_{\text{CO2}}(T) + \nu_{\text{H2}}\bar{g}^*_{\text{H2}}(T) - \nu_{\text{CO}}\bar{g}^*_{\text{CO}}(T) - \nu_{\text{H2O}}\bar{g}^*_{\text{H2O}}(T)$$

At 2500 K,

$$\begin{aligned}
\Delta G^*(T) &= \nu_{\text{CO2}}\bar{g}^*_{\text{CO2}}(T) + \nu_{\text{H2}}\bar{g}^*_{\text{H2}}(T) - \nu_{\text{CO}}\bar{g}^*_{\text{CO}}(T) - \nu_{\text{H2O}}\bar{g}^*_{\text{H2O}}(T) \\
&= \nu_{\text{CO2}}(\bar{h} - T\bar{s})_{\text{CO2}} + \nu_{\text{H2}}(\bar{h} - T\bar{s})_{\text{H2}} - \nu_{\text{CO}}(\bar{h} - T\bar{s})_{\text{CO}} - \nu_{\text{H2O}}(\bar{h} - T\bar{s})_{\text{H2O}} \\
&= 1[(-271{,}641) - (2500)(322.60)] + 1[(70{,}452) - (2500)(196.10)] \\
&\quad -1[(-35{,}510) - (2500)(266.65)] - 1[(-142{,}891) - (2500)(276.18)] \\
&= 37{,}525 \text{ kJ/kmol}
\end{aligned}$$

The enthalpies at 2500 K and entropies at 2500 K and 101.3 kPa (1 atm) are obtained from EES. Substituting,

$$\ln K_p = -\frac{37{,}525 \text{ kJ/kmol}}{(8.314 \text{ kJ/kmol}\cdot\text{K})(2500 \text{ K})} = -1.8054 \longrightarrow K_p = \mathbf{0.1644}$$

The equilibrium constant may be estimated using the integrated van't Hoff equation:

$$\ln\left(\frac{K_{p,\text{est}}}{K_{p1}}\right) = \frac{\bar{h}_R}{R_u}\left(\frac{1}{T_R} - \frac{1}{T}\right)$$

$$\ln\left(\frac{K_{p,\text{est}}}{0.2209}\right) = \frac{-26{,}176 \text{ kJ/kmol}}{8.314 \text{ kJ/kmol.K}}\left(\frac{1}{2000 \text{ K}} - \frac{1}{2500 \text{ K}}\right) \longrightarrow K_{p,\text{est}} = \mathbf{0.1612}$$

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16-44 A constant volume tank contains a mixture of H2 and O2. The contents are ignited. The final temperature and pressure in the tank are to be determined.

Analysis The reaction equation with products in equilibrium is

$$\mathrm{H_2} + \mathrm{O_2} \longrightarrow a\,\mathrm{H_2} + b\,\mathrm{H_2O} + c\,\mathrm{O_2}$$

The coefficients are determined from the mass balances

Hydrogen balance: $2 = 2a + 2b$

Oxygen balance: $2 = b + 2c$

The assumed equilibrium reaction is

$$\mathrm{H_2O} \longleftrightarrow \mathrm{H_2} + 0.5\mathrm{O_2}$$

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

$$\Delta G^*(T) = \nu_{\mathrm{H2}}\,\bar{g}^*_{\mathrm{H2}}(T_{\mathrm{prod}}) + \nu_{\mathrm{O2}}\,\bar{g}^*_{\mathrm{O2}}(T_{\mathrm{prod}}) - \nu_{\mathrm{H2O}}\,\bar{g}^*_{\mathrm{H2O}}(T_{\mathrm{prod}})$$

and the Gibbs functions are given by

$$\bar{g}^*_{\mathrm{H2}}(T_{\mathrm{prod}}) = (\bar{h} - T_{\mathrm{prod}}\bar{s})_{\mathrm{H2}}$$
$$\bar{g}^*_{\mathrm{O2}}(T_{\mathrm{prod}}) = (\bar{h} - T_{\mathrm{prod}}\bar{s})_{\mathrm{O2}}$$
$$\bar{g}^*_{\mathrm{H2O}}(T_{\mathrm{prod}}) = (\bar{h} - T_{\mathrm{prod}}\bar{s})_{\mathrm{H2O}}$$

The equilibrium constant is also given by

$$K_p = \frac{a^1 c^{0.5}}{b^1}\left(\frac{P}{N_{\mathrm{tot}}}\right)^{1+0.5-1} = \frac{ac^{0.5}}{b}\left(\frac{P_2/101.3}{a+b+c}\right)^{0.5}$$

An energy balance on the tank under adiabatic conditions gives

$$U_R = U_P$$

where

$$U_R = 1(\bar{h}_{\mathrm{H2@25°C}} - R_u T_{\mathrm{reac}}) + 1(\bar{h}_{\mathrm{O2@25°C}} - R_u T_{\mathrm{reac}})$$
$$= 0 - (8.314\ \mathrm{kJ/kmol.K})(298.15\ \mathrm{K}) + 0 - (8.314\ \mathrm{kJ/kmol.K})(298.15\ \mathrm{K}) = -4958\ \mathrm{kJ/kmol}$$
$$U_P = a(\bar{h}_{\mathrm{H2@}T_{\mathrm{prod}}} - R_u T_{\mathrm{prod}}) + b(\bar{h}_{\mathrm{H2O@}T_{\mathrm{prod}}} - R_u T_{\mathrm{prod}}) + c(\bar{h}_{\mathrm{O2@}T_{\mathrm{prod}}} - R_u T_{\mathrm{prod}})$$

The relation for the final pressure is

$$P_2 = \frac{N_{\mathrm{tot}}}{N_1}\frac{T_{\mathrm{prod}}}{T_{\mathrm{reac}}}P_1 = \left(\frac{a+b+c}{2}\right)\left(\frac{T_{\mathrm{prod}}}{298.15\ \mathrm{K}}\right)(101.3\ \mathrm{kPa})$$

Solving all the equations simultaneously using EES, we obtain the final temperature and pressure in the tank to be

$$T_{\mathrm{prod}} = \mathbf{3857\ K}$$
$$P_2 = \mathbf{1043\ kPa}$$

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Simultaneous Reactions

16-45C It can be expresses as "$(dG)_{T,P} = 0$ for each reaction." Or as "the K_p relation for each reaction must be satisfied."

16-46C The number of K_p relations needed to determine the equilibrium composition of a reacting mixture is equal to the difference between the number of species present in the equilibrium mixture and the number of elements.

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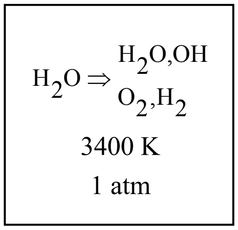
16-47 Two chemical reactions are occurring in a mixture. The equilibrium composition at a specified temperature is to be determined.



Assumptions **1** The equilibrium composition consists of H_2O, 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

$$H_2O \longrightarrow x\,H_2O + y\,H_2 + z\,O_2 + w\,OH$$

Mass balances for hydrogen and oxygen yield

H balance: $2 = 2x + 2y + w$ (1)

O balance: $1 = x + 2z + w$ (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

$$H_2O \Leftrightarrow H_2 + \tfrac{1}{2}O_2 \qquad \text{(reaction 1)}$$

$$H_2O \Leftrightarrow \tfrac{1}{2}H_2 + OH \qquad \text{(reaction 2)}$$

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

$$\ln K_{P1} = -1.891 \longrightarrow K_{P1} = 0.15092$$

$$\ln K_{P2} = -1.576 \longrightarrow K_{P2} = 0.20680$$

The K_p relations for these two simultaneous reactions are

$$K_{P1} = \frac{N_{H_2}^{\nu_{H_2}} N_{O_2}^{\nu_{O_2}}}{N_{H_2O}^{\nu_{H_2O}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{H_2}+\nu_{O_2}-\nu_{H_2O})} \quad \text{and} \quad K_{P2} = \frac{N_{H_2}^{\nu_{H_2}} N_{OH}^{\nu_{OH}}}{N_{H_2O}^{\nu_{H_2O}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{H_2}+\nu_{OH}-\nu_{H_2O})}$$

where $N_{\text{total}} = N_{H_2O} + N_{H_2} + N_{O_2} + N_{OH} = x + y + z + w$

Substituting,

$$0.15092 = \frac{(y)(z)^{1/2}}{x}\left(\frac{1}{x+y+z+w}\right)^{1/2} \qquad (3)$$

$$0.20680 = \frac{(w)(y)^{1/2}}{x}\left(\frac{1}{x+y+z+w}\right)^{1/2} \qquad (4)$$

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

$x = 0.574$ $y = 0.308$ $z = 0.095$ $w = 0.236$

Therefore, the equilibrium composition becomes

$$\mathbf{0.574H_2O + 0.308H_2 + 0.095O_2 + 0.236OH}$$

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16-48 Two chemical reactions are occurring in a mixture. The equilibrium composition at a specified temperature 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

CO_2, CO, O_2, O
3200 K
2 atm

$$2\,CO_2 + O_2 \longrightarrow x\,CO_2 + y\,CO + z\,O_2 + w\,O$$

Mass balances for carbon and oxygen yield

C balance: $2 = x + y$ (1)

O balance: $6 = 2x + y + 2z + w$ (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

$CO_2 \Leftrightarrow CO + \frac{1}{2}O_2$ (reaction 1)

$O_2 \Leftrightarrow 2O$ (reaction 2)

The equilibrium constant for these two reactions at 3200 K are determined from Table A-28 to be

$$\ln K_{P1} = -0.429 \longrightarrow K_{P1} = 0.65116$$

$$\ln K_{P2} = -3.072 \longrightarrow K_{P2} = 0.04633$$

The K_P relations for these two simultaneous reactions are

$$K_{P1} = \frac{N_{CO}^{\nu_{CO}} N_{O_2}^{\nu_{O_2}}}{N_{CO_2}^{\nu_{CO_2}}}\left(\frac{P}{N_{total}}\right)^{(\nu_{CO}+\nu_{O_2}-\nu_{CO_2})}$$

$$K_{P2} = \frac{N_{O}^{\nu_{O}}}{N_{O_2}^{\nu_{O_2}}}\left(\frac{P}{N_{total}}\right)^{\nu_{O}-\nu_{O_2}}$$

where

$$N_{total} = N_{CO_2} + N_{O_2} + N_{CO} + N_{O} = x + y + z + w$$

Substituting,

$$0.65116 = \frac{(y)(z)^{1/2}}{x}\left(\frac{2}{x+y+z+w}\right)^{1/2} \quad (3)$$

$$0.04633 = \frac{w^2}{z}\left(\frac{2}{x+y+z+w}\right)^{2-1} \quad (4)$$

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

$x = 1.127$ $y = 0.873$ $z = 1.273$ $w = 0.326$

Thus the equilibrium composition is

$$\mathbf{1.127CO_2 + 0.873CO + 1.273O_2 + 0.326O}$$

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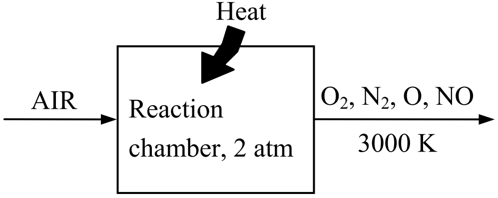
16-49 Two chemical reactions are occurring at high-temperature air. The equilibrium composition at a specified temperature is to be determined.

Assumptions **1** The equilibrium composition consists of O_2, N_2, O, and NO. **2** The constituents of the mixture are ideal gases.

Analysis The reaction equation during this process can be expressed as



$$O_2 + 3.76N_2 \longrightarrow xN_2 + yNO + zO_2 + wO$$

Mass balances for nitrogen and oxygen yield

N balance: $7.52 = 2x + y$ (1)

O balance: $2 = y + 2z + w$ (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

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \Leftrightarrow NO \qquad \text{(reaction 1)}$$

$$O_2 \Leftrightarrow 2O \qquad \text{(reaction 2)}$$

The equilibrium constant for these two reactions at 3000 K are determined from Table A-28 to be

$$\ln K_{P1} = -2.114 \longrightarrow K_{P1} = 0.12075$$

$$\ln K_{P2} = -4.357 \longrightarrow K_{P2} = 0.01282$$

The K_P relations for these two simultaneous reactions are

$$K_{P1} = \frac{N_{NO}^{\nu_{NO}}}{N_{N_2}^{\nu_{N_2}} N_{O_2}^{\nu_{O_2}}}\left(\frac{P}{N_{total}}\right)^{(\nu_{NO}-\nu_{N_2}-\nu_{O_2})}$$

$$K_{P2} = \frac{N_O^{\nu_O}}{N_{O_2}^{\nu_{O_2}}}\left(\frac{P}{N_{total}}\right)^{\nu_O-\nu_{O_2}}$$

where $N_{total} = N_{N_2} + N_{NO} + N_{O_2} + N_O = x + y + z + w$

Substituting,

$$0.12075 = \frac{y}{x^{0.5}z^{0.5}}\left(\frac{2}{x+y+z+w}\right)^{1-0.5-0.5} \qquad (3)$$

$$0.01282 = \frac{w^2}{z}\left(\frac{2}{x+y+z+w}\right)^{2-1} \qquad (4)$$

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

$x = 3.656$ $y = 0.2086$ $z = 0.8162$ $w = 0.1591$

Thus the equilibrium composition is

$$\mathbf{3.656N_2 + 0.2086NO + 0.8162O_2 + 0.1591O}$$

The equilibrium constant of the reaction $N_2 \Leftrightarrow 2N$ at 3000 K is $\ln K_P = -22.359$, which is much smaller than the K_P values of the reactions considered. Therefore, it is reasonable to assume that no N will be present in the equilibrium mixture.

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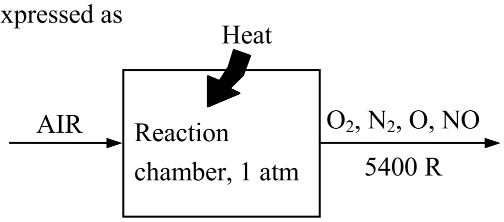
16-50E [*Also solved by EES on enclosed CD*] Two chemical reactions are occurring in air. The equilibrium composition at a specified temperature is to be determined.

Assumptions **1** The equilibrium composition consists of O_2, N_2, O, and NO. **2** The constituents of the mixture are ideal gases.

Analysis The reaction equation during this process can be expressed as



$$O_2 + 3.76\,N_2 \longrightarrow x\,N_2 + y\,NO + z\,O_2 + w\,O$$

Mass balances for nitrogen and oxygen yield

N balance: $7.52 = 2x + y$ (1)

O balance: $2 = y + 2z + w$ (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

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \Leftrightarrow NO \qquad \text{(reaction 1)}$$

$$O_2 \Leftrightarrow 2O \qquad \text{(reaction 2)}$$

The equilibrium constant for these two reactions at $T = 5400$ R = 3000 K are determined from Table A-28 to be

$$\ln K_{P1} = -2.114 \longrightarrow K_{P1} = 0.12075$$

$$\ln K_{P2} = -4.357 \longrightarrow K_{P2} = 0.01282$$

The K_P relations for these two simultaneous reactions are

$$K_{P1} = \frac{N_{NO}^{\nu_{NO}}}{N_{N_2}^{\nu_{N_2}} N_{O_2}^{\nu_{O_2}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{NO}-\nu_{N_2}-\nu_{O_2})}$$

$$K_{P2} = \frac{N_{O}^{\nu_{O}}}{N_{O_2}^{\nu_{O_2}}}\left(\frac{P}{N_{\text{total}}}\right)^{\nu_O-\nu_{O_2}}$$

where $N_{\text{total}} = N_{N_2} + N_{NO} + N_{O_2} + N_O = x + y + z + w$

Substituting,

$$0.12075 = \frac{y}{x^{0.5}z^{0.5}}\left(\frac{1}{x+y+z+w}\right)^{1-0.5-0.5} \qquad (3)$$

$$0.01282 = \frac{w^2}{z}\left(\frac{1}{x+y+z+w}\right)^{2-1} \qquad (4)$$

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

$x = 3.658$ $y = 0.2048$ $z = 0.7868$ $w = 0.2216$

Thus the equilibrium composition is

$$\mathbf{3.658N_2 + 0.2048NO + 0.7868O_2 + 0.2216O}$$

The equilibrium constant of the reaction $N_2 \Leftrightarrow 2N$ at 5400 R is $\ln K_P = -22.359$, which is much smaller than the K_P values of the reactions considered. Therefore, it is reasonable to assume that no N will be present in the equilibrium mixture.

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14-51E EES Problem 16-50E is reconsidered. Using EES (or other) software, the equilibrium solution is to be obtained by minimizing the Gibbs function by using the optimization capabilities built into EES. This solution technique is to be compared with that used in the previous problem.

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

```
"This example illustrates how EES can be used to solve multi-reaction chemical equilibria
problems by directly minimizing the Gibbs function.

          0.21 O2+0.79 N2 = a O2+b O + c N2 + d NO

Two of the four coefficients, a, b, c, and d, are found by minimiming the Gibbs function at a total
pressure of 1 atm and a temperature of 5400 R.  The other two are found from mass balances.

The equilibrium solution can be found by applying the Law of Mass Action to two
simultaneous equilibrium reactions or by minimizing the Gibbs function.  In this problem, the
Gibbs function is directly minimized using the optimization capabilities built into EES.

To run this program, select MinMax from the Calculate menu.  There are four compounds present
in the products subject to two elemental balances, so there are two degrees of freedom.
Minimize
Gibbs with respect to two molar quantities such as coefficients b and d.  The equilibrium mole
numbers of each specie will be determined and displayed in the Solution window.

Minimizing the Gibbs function to find the equilibrium composition requires good initial guesses."

"Data from Data Input Window"
{T=5400 "R"
P=1 "atm" }

AO2=0.21; BN2=0.79 "Composition  of air"
AO2*2=a*2+b+d "Oxygen balance"
BN2*2=c*2+d "Nitrogen balance"

"The total moles at equilibrium are"
N_tot=a+b+c+d
y_O2=a/N_tot;  y_O=b/N_tot; y_N2=c/N_tot; y_NO=d/N_tot

"The following equations provide the specific Gibbs function for three of the components."
g_O2=Enthalpy(O2,T=T)-T*Entropy(O2,T=T,P=P*y_O2)
g_N2=Enthalpy(N2,T=T)-T*Entropy(N2,T=T,P=P*y_N2)
g_NO=Enthalpy(NO,T=T)-T*Entropy(NO,T=T,P=P*y_NO)
"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 kgmole, K, and kJ so we must convert h and s to English units."
T_K=T*Convert(R,K) "Convert R to K"
Call JANAF('O',T_K:Cp`,h`,S`) "Units from JANAF are SI"
S_O=S`*Convert(kJ/kgmole-K, Btu/lbmole-R)
h_O=h`*Convert(kJ/kgmole, Btu/lbmole)
 "The entropy from JANAF is for one atmosphere so it must be corrected for partial pressure."
g_O=h_O-T*(S_O-R_u*ln(Y_O))
R_u=1.9858 "The universal gas constant in Btu/mole-R "
"The extensive Gibbs function is the sum of the products of the specific Gibbs function and the
molar amount of each substance."
Gibbs=a*g_O2+b*g_O+c*g_N2+d*g_NO
```

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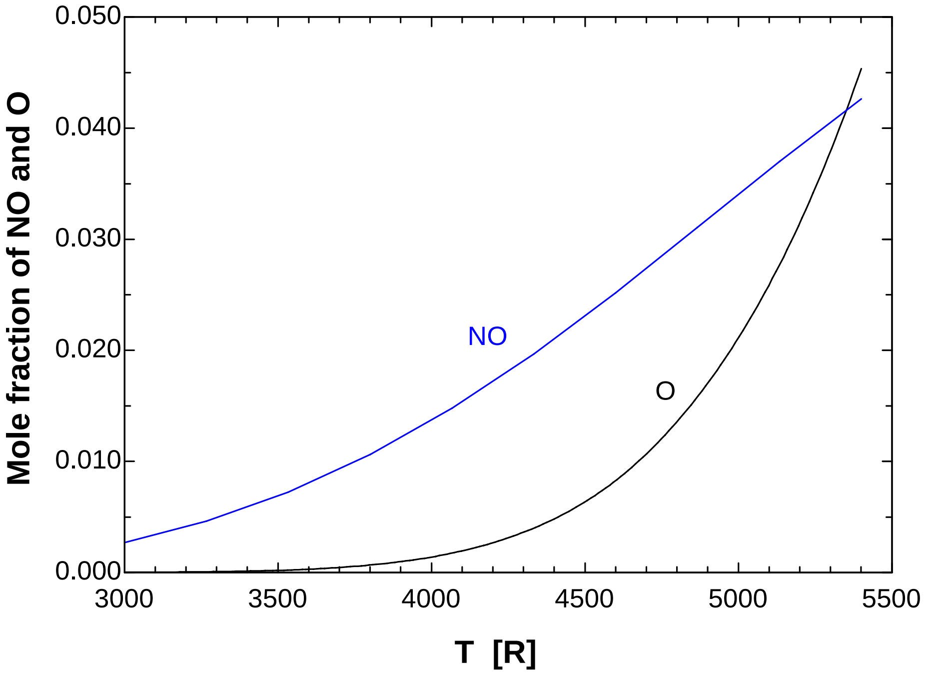
d [lbmol]	b [lbmol]	Gibbs [Btu/lbmol]	y_{O2}	y_O	y_{NO}	y_{N2}	T [R]
0.002698	0.00001424	-162121	0.2086	0.0000	0.0027	0.7886	3000
0.004616	0.00006354	-178354	0.2077	0.0001	0.0046	0.7877	3267
0.007239	0.0002268	-194782	0.2062	0.0002	0.0072	0.7863	3533
0.01063	0.000677	-211395	0.2043	0.0007	0.0106	0.7844	3800
0.01481	0.001748	-228188	0.2015	0.0017	0.0148	0.7819	4067
0.01972	0.004009	-245157	0.1977	0.0040	0.0197	0.7786	4333
0.02527	0.008321	-262306	0.1924	0.0083	0.0252	0.7741	4600
0.03132	0.01596	-279641	0.1849	0.0158	0.0311	0.7682	4867
0.03751	0.02807	-297179	0.1748	0.0277	0.0370	0.7606	5133
0.04361	0.04641	-314941	0.1613	0.0454	0.0426	0.7508	5400



Discussion The equilibrium composition in the above table are based on the reaction in which the reactants are 0.21 kmol O_2 and 0.79 kmol N_2. If you multiply the equilibrium composition mole numbers above with 4.76, you will obtain equilibrium composition for the reaction in which the reactants are 1 kmol O_2 and 3.76 kmol N_2.This is the case in problem 16-43E.

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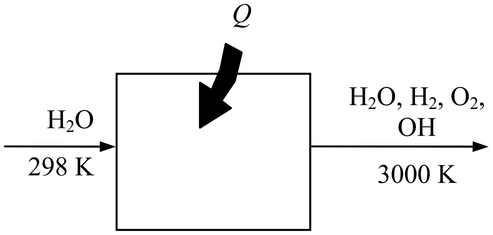
16-52 Water vapor is heated during a steady-flow process. The rate of heat supply for a specified exit temperature is to be determined for two cases.

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

Analysis (*a*) Assuming some H_2O dissociates into H_2, O_2, and O, the dissociation equation can be written as



$$H_2O \longrightarrow x\,H_2O + y\,H_2 + z\,O_2 + w\,OH$$

Mass balances for hydrogen and oxygen yield

H balance: $2 = 2x + 2y + w$ (1)

O balance: $1 = x + 2z + w$ (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

$$H_2O \Leftrightarrow H_2 + \tfrac{1}{2}O_2 \qquad \text{(reaction 1)}$$

$$H_2O \Leftrightarrow \tfrac{1}{2}H_2 + OH \qquad \text{(reaction 2)}$$

The equilibrium constant for these two reactions at 3000 K are determined from Table A-28 to be

$$\ln K_{P1} = -3.086 \longrightarrow K_{P1} = 0.04568$$

$$\ln K_{P2} = -2.937 \longrightarrow K_{P2} = 0.05302$$

The K_P relations for these three simultaneous reactions are

$$K_{P1} = \frac{N_{H_2}^{\nu_{H_2}} N_{O_2}^{\nu_{O_2}}}{N_{H_2O}^{\nu_{H_2O}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{H_2}+\nu_{O_2}-\nu_{H_2O})}$$

$$K_{P2} = \frac{N_{H_2}^{\nu_{H_2}} N_{OH}^{\nu_{OH}}}{N_{H_2O}^{\nu_{H_2O}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{H_2}+\nu_{O_2}-\nu_{H_2O})}$$

where

$$N_{\text{total}} = N_{H_2O} + N_{H_2} + N_{O_2} + N_{OH} = x + y + z + w$$

Substituting,

$$0.04568 = \frac{(y)(z)^{1/2}}{x}\left(\frac{1}{x+y+z+w}\right)^{1/2} \qquad (3)$$

$$0.05302 = \frac{(w)(y)^{1/2}}{x}\left(\frac{1}{x+y+z+w}\right)^{1/2} \qquad (4)$$

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

$x = 0.784$ $y = 0.162$ $z = 0.054$ $w = 0.108$

Thus the balanced equation for the dissociation reaction is

$$H_2O \longrightarrow 0.784H_2O + 0.162H_2 + 0.054O_2 + 0.108OH$$

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The heat transfer for this dissociation process is determined from the steady-flow energy balance $E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$ with $W = 0$,

$$Q_{\text{in}} = \sum N_P\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_P - \sum N_R\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_R$$

Assuming the O_2 and O to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\bar{\mathbf{h}}_\mathbf{f}^\circ$ **kJ/kmol**	$\bar{\mathbf{h}}_{\mathbf{298\ K}}$ **kJ/kmol**	$\bar{\mathbf{h}}_{\mathbf{3000\ K}}$ **kJ/kmol**
H_2O	-241,820	9904	136,264
H_2	0	8468	97,211
O_2	0	8682	106,780
OH	39,460	9188	98,763

Substituting,

$$\begin{aligned} Q_{\text{in}} &= 0.784(-241{,}820 + 136{,}264 - 9904) \\ &\quad + 0.162(0 + 97{,}211 - 8468) \\ &\quad + 0.054(0 + 106{,}780 - 8682) \\ &\quad + 0.108(39{,}460 + 98{,}763 - 9188) - (-241{,}820) \\ &= 184{,}909 \text{ kJ / kmol } H_2O \end{aligned}$$

The mass flow rate of H_2O can be expressed in terms of the mole numbers as

$$\dot{N} = \frac{\dot{m}}{M} = \frac{0.2 \text{ kg / min}}{18 \text{ kg / kmol}} = 0.01111 \text{ kmol / min}$$

Thus,

$$\dot{Q}_{\text{in}} = \dot{N} \times Q_{\text{in}} = (0.01111 \text{ kmol/min})(184{,}909 \text{ kJ/kmol}) = \mathbf{2055\ kJ/min}$$

(*b*) If no dissociates takes place, then the process involves no chemical reactions and the heat transfer can be determined from the steady-flow energy balance for nonreacting systems to be

$$\begin{aligned} \dot{Q}_{\text{in}} &= \dot{m}(h_2 - h_1) = \dot{N}(\bar{h}_2 - \bar{h}_1) \\ &= (0.01111 \text{ kmol / min})(136{,}264 - 9904) \text{ kJ / kmol} \\ &= \mathbf{1404\ kJ / min} \end{aligned}$$

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16-53 EES Problem 16-52 is reconsidered. The effect of the final temperature on the rate of heat supplied for the two cases is to be studied.

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

```
"This example illustrates how EES can be used to solve multi-reaction chemical equilibria
problems by directly minimizing the Gibbs function.

            H2O = x H2O+y H2+z O2 + w OH

Two of the four coefficients, x, y, z, and w are found by minimiming the Gibbs function at a total
pressure of 1 atm and a temperature of 3000 K.  The other two are found from mass balances.

The equilibrium solution can be found by applying the Law of Mass Action (Eq. 15-15) to two
simultaneous equilibrium reactions or by minimizing the Gibbs function.  In this problem, the
Gibbs function is directly minimized using the optimization capabilities built into EES.

To run this program, click on the Min/Max icon.  There are four compounds present
in the products subject to two elemental balances, so there are two degrees of freedom.
Minimize Gibbs with respect to two molar quantities such as coefficient z and w.  The
equilibrium mole numbers of each specie will be determined and displayed in the
Solution window.

Minimizing the Gibbs function to find the equilibrium composition requires good initial
guesses."

"T_Prod=3000 [K]"
P=101.325 [kPa]
m_dot_H2O = 0.2 [kg/min]
T_reac = 298 [K]
T = T_prod
P_atm=101.325 [kPa]

"H2O = x H2O+y H2+z O2 + w OH"
AH2O=1 "Solution for 1 mole of water"
AH2O=x+z*2+w "Oxygen balance"
AH2O*2=x*2+y*2+w "Hydrogen balance"

"The total moles at equilibrium are"
N_tot=x+y+z+w
y_H2O=x/N_tot;  y_H2=y/N_tot; y_O2=z/N_tot; y_OH=w/N_tot

"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 kgmole, K, and kJ."

Call JANAF('OH',T_prod:Cp`,h`,S`) "Units from JANAF are SI"
S_OH=S`
h_OH=h`
 "The entropy from JANAF is for one atmosphere so it must be corrected for partial pressure."
g_OH=h_OH-T_prod*(S_OH-R_u*ln(y_OH*P/P_atm))
R_u=8.314  "The universal gas constant in kJ/kmol-K "

"The following equations provide the specific Gibbs function for three of the components."
g_O2=Enthalpy(O2,T=T_prod)-T_prod*Entropy(O2,T=T_prod,P=P*y_O2)
g_H2=Enthalpy(H2,T=T_prod)-T_prod*Entropy(H2,T=T_prod,P=P*y_H2)
```

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g_H2O=Enthalpy(H2O,T=T_prod)-T_prod*Entropy(H2O,T=T_prod,P=P*y_H2O)

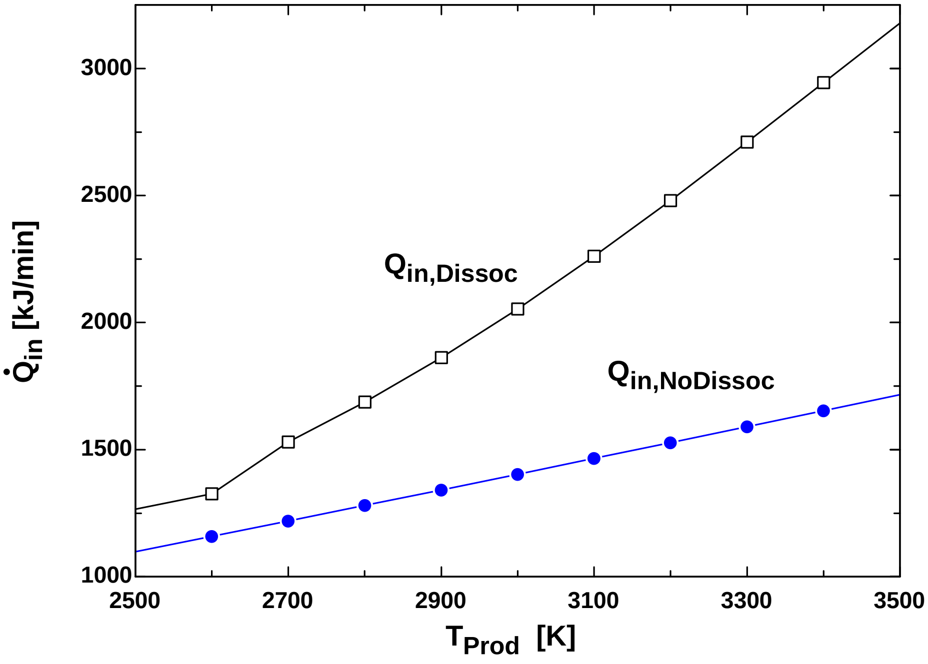
"The extensive Gibbs function is the sum of the products of the specific Gibbs function and the
molar amount of each substance."
Gibbs=x*g_H2O+y*g_H2+z*g_O2+w*g_OH

"H2O = x H2O+y H2+z O2 + w OH"

1*Enthalpy(H2O,T=T_reac)+Q_in=x*Enthalpy(H2O,T=T_prod)+y*Enthalpy(H2,T=T_prod)+z*Enthalpy(O2,T=T_prod)+w*h_OH

N_dot_H2O = m_dot_H2O/molarmass(H2O)
Q_dot_in_Dissoc = N_dot_H2O*Q_in
Q_dot_in_NoDissoc = N_dot_H2O*(Enthalpy(H2O,T=T_prod) - Enthalpy(H2O,T=T_reac))
```

T_{prod} [K]	$Q_{in,Dissoc}$ [kJ/min]	$Q_{in,NoDissoc}$ [kJ/min]
2500	1266	1098
2600	1326	1158
2700	1529	1219
2800	1687	1280
2900	1862	1341
3000	2053	1403
3100	2260	1465
3200	2480	1528
3300	2710	1590
3400	2944	1653
3500	3178	1716



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16-54 EES Ethyl alcohol C_2H_5OH (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

$$C_2H_5OH\,(\text{gas}) + (1+Ex)a_{\text{th}}\left[O_2 + 3.76N_2\right] \longrightarrow 2\,CO_2 + 3\,H_2O + (Ex)(a_{\text{th}})\,O_2 + f\,N_2$$

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

$$1 + (1+Ex)a_{\text{th}} \times 2 = 2\times 2 + 3\times 1 + (Ex)(a_{\text{th}})\times 2$$

The reaction equation with products in equilibrium is

$$C_2H_5OH\,(\text{gas}) + (1+Ex)a_{\text{th}}\left[O_2 + 3.76N_2\right] \longrightarrow a\,CO_2 + b\,CO + d\,H_2O + e\,O_2 + f\,N_2 + g\,NO$$

The coefficients are determined from the mass balances

Carbon balance: $2 = a + b$

Hydrogen balance: $6 = 2d \longrightarrow d = 3$

Oxygen balance: $1 + (1+Ex)a_{\text{th}} \times 2 = a\times 2 + b + d + e\times 2 + g$

Nitrogen balance: $(1+Ex)a_{\text{th}} \times 3.76 \times 2 = f \times 2 + g$

Solving the above equations, we find the coefficients to be

$$Ex = 0.4,\ a_{\text{th}} = 3,\ \ a = 1.995,\ \ b = 0.004712,\ \ d = 3,\ \ e = 1.17,\ f = 15.76,\ \ g = 0.06428$$

Then, we write the balanced reaction equation as

$$C_2H_5OH\,(\text{gas}) + 4.2\left[O_2 + 3.76N_2\right]$$
$$\longrightarrow 1.995\,CO_2 + 0.004712\,CO + 3\,H_2O + 1.17\,O_2 + 15.76\,N_2 + 0.06428\,NO$$

Total moles of products at equilibrium are

$$N_{\text{tot}} = 1.995 + 0.004712 + 3 + 1.17 + 15.76 = 21.99$$

The first assumed equilibrium reaction is

$$CO_2 \longleftrightarrow CO + 0.5O_2$$

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

$$K_{p1} = \exp\left(\frac{-\Delta G_1{}^*(T_{\text{prod}})}{R_u T_{\text{prod}}}\right)$$

Where $\Delta G_1{}^*(T_{\text{prod}}) = \nu_{\text{CO}}\overline{g}^*_{\text{CO}}(T_{\text{prod}}) + \nu_{\text{O2}}\overline{g}^*_{\text{O2}}(T_{\text{prod}}) - \nu_{\text{CO2}}\overline{g}^*_{\text{CO2}}(T_{\text{prod}})$

and the Gibbs functions are defined as

$$\overline{g}^*_{\text{CO}}(T_{\text{prod}}) = (\overline{h} - T_{\text{prod}}\overline{s})_{\text{CO}}$$
$$\overline{g}^*_{\text{O2}}(T_{\text{prod}}) = (\overline{h} - T_{\text{prod}}\overline{s})_{\text{O2}}$$
$$\overline{g}^*_{\text{CO2}}(T_{\text{prod}}) = (\overline{h} - T_{\text{prod}}\overline{s})_{\text{CO2}}$$

The equilibrium constant is also given by

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$$K_{p1} = \frac{be^{0.5}}{a}\left(\frac{P}{N_{\text{tot}}}\right)^{1+0.5-1} = \frac{(0.004712)(1.17)^{0.5}}{1.995}\left(\frac{1}{21.99}\right)^{0.5} = 0.0005447$$

The second assumed equilibrium reaction is

$$0.5\text{N}_2 + 0.5\text{O}_2 \longleftrightarrow \text{NO}$$

Also, for this reaction, we have

$$\bar{g}^*_{\text{NO}}(T_{\text{prod}}) = (\bar{h} - T_{\text{prod}}\bar{s})_{\text{NO}}$$

$$\bar{g}^*_{\text{N2}}(T_{\text{prod}}) = (\bar{h} - T_{\text{prod}}\bar{s})_{\text{N2}}$$

$$\bar{g}^*_{\text{O2}}(T_{\text{prod}}) = (\bar{h} - T_{\text{prod}}\bar{s})_{\text{O2}}$$

$$\Delta G_2{}^*(T_{\text{prod}}) = \nu_{\text{NO}}\bar{g}^*_{\text{NO}}(T_{\text{prod}}) - \nu_{\text{N2}}\bar{g}^*_{\text{N2}}(T_{\text{prod}}) - \nu_{\text{O2}}\bar{g}^*_{\text{O2}}(T_{\text{prod}})$$

$$K_{p2} = \exp\left(\frac{-\Delta G_2{}^*(T_{\text{prod}})}{R_u T_{\text{prod}}}\right)$$

$$K_{p2} = \left(\frac{P}{N_{\text{tot}}}\right)^{1-0.5-0.5}\frac{g}{e^{0.5}f^{0.5}} = \left(\frac{1}{21.99}\right)^0\frac{0.06428}{(1.17)^{0.5}(15.76)^{0.5}} = 0.01497$$

A steady flow energy balance gives

$$H_R = H_P$$

where

$$\begin{aligned} H_R &= \bar{h}^o_{f\ \text{fuel@25°C}} + 4.2\bar{h}_{\text{O2@25°C}} + 15.79\bar{h}_{\text{N2@25°C}} \\ &= (-235{,}310\text{ kJ/kmol}) + 4.2(0) + 15.79(0) = -235{,}310\text{ kJ/kmol} \end{aligned}$$

$$\begin{aligned} H_P &= 1.995\bar{h}_{\text{CO2@}T_{\text{prod}}} + 0.004712\bar{h}_{\text{CO@}T_{\text{prod}}} + 3\bar{h}_{\text{H2O@}T_{\text{prod}}} + 1.17\bar{h}_{\text{O2@}T_{\text{prod}}} \\ &\quad + 15.76\bar{h}_{\text{N2@}T_{\text{prod}}} + 0.06428\bar{h}_{\text{NO@}T_{\text{prod}}} \end{aligned}$$

Solving the energy balance equation using EES, we obtain the adiabatic flame temperature

$$T_{\text{prod}} = \mathbf{1901\ K}$$

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

```
"The reactant temperature is:"
T_reac= 25+273 "[K]"
"For adiabatic combustion of 1 kmol of fuel: "
Q_out = 0 "[kJ]"
PercentEx = 40  "Percent excess air"
Ex = PercentEx/100  "EX = % Excess air/100"
P_prod =101.3"[kPa]"
R_u=8.314 "[kJ/kmol-K]"
"The complete combustion reaction equation for excess air  is:"
"C2H5OH(gas)+ (1+Ex)*A_th (O2 +3.76N2)=2 CO2 +  3 H2O + Ex*A_th O2 + f N2 "
"Oxygen Balance for complete combustion:"
1 + (1+Ex)*A_th*2=2*2+3*1 + Ex*A_th*2
"The reaction equation for excess air and products in equilibrium is:"
"C2H5OH(gas)+ (1+Ex)*A_th (O2 +3.76N2)=a CO2 + b CO+ d H2O + e O2 + f N2 + g NO"
```

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"Carbon Balance:"
2=a + b
"Hydrogen Balance:"
6=2*d
"Oxygen Balance:"
1 + (1+Ex)*A_th*2=a*2+b + d + e*2 +g
"Nitrogen Balance:"
(1+Ex)*A_th*3.76 *2= f*2 + g
N_tot =a +b + d + e + f +g "Total kilomoles of products at equilibrium"
"The first 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=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)
"The standard-state Gibbs function is"
DELTAG_1 =1*g_CO+0.5*g_O2-1*g_CO2
"The equilibrium constant is given by Eq. 15-14."
K_P_1  = exp(-DELTAG_1 /(R_u*T_prod ))
P=P_prod /101.3"atm"
"The equilibrium constant is also given by Eq. 15-15."
"K_ P_1 = (P/N_tot)^(1+0.5-1)*(b^1*e^0.5)/(a^1)"
sqrt(P/N_tot) *b *sqrt(e) =K_P_1*a
"The econd assumed equilibrium reaction is 0.5N2+0.5O2=NO"
g_NO=Enthalpy(NO,T=T_prod )-T_prod *Entropy(NO,T=T_prod ,P=101.3)
g_N2=Enthalpy(N2,T=T_prod )-T_prod *Entropy(N2,T=T_prod ,P=101.3)
"The standard-state Gibbs function is"
DELTAG_2 =1*g_NO-0.5*g_O2-0.5*g_N2
"The equilibrium constant is given by Eq. 15-14."
K_P_2  = exp(-DELTAG_2 /(R_u*T_prod ))
"The equilibrium constant is also given by Eq. 15-15."
"K_ P_2 = (P/N_tot)^(1-0.5-0.5)*(g^1)/(e^0.5*f^0.5)"
g=K_P_2 *sqrt(e*f)
"The steady-flow energy balance is:"
H_R = Q_out+H_P
h_bar_f_C2H5OHgas=-235310 "[kJ/kmol]"
H_R=1*(h_bar_f_C2H5OHgas )
+(1+Ex)*A_th*ENTHALPY(O2,T=T_reac)+(1+Ex)*A_th*3.76*ENTHALPY(N2,T=T_reac)
"[kJ/kmol]"
H_P=a*ENTHALPY(CO2,T=T_prod)+b*ENTHALPY(CO,T=T_prod)+d*ENTHALPY(H2O,T=T_pro
d)+e*ENTHALPY(O2,T=T_prod)+f*ENTHALPY(N2,T=T_prod)+g*ENTHALPY(NO,T=T_prod)
"[kJ/kmol]"
```

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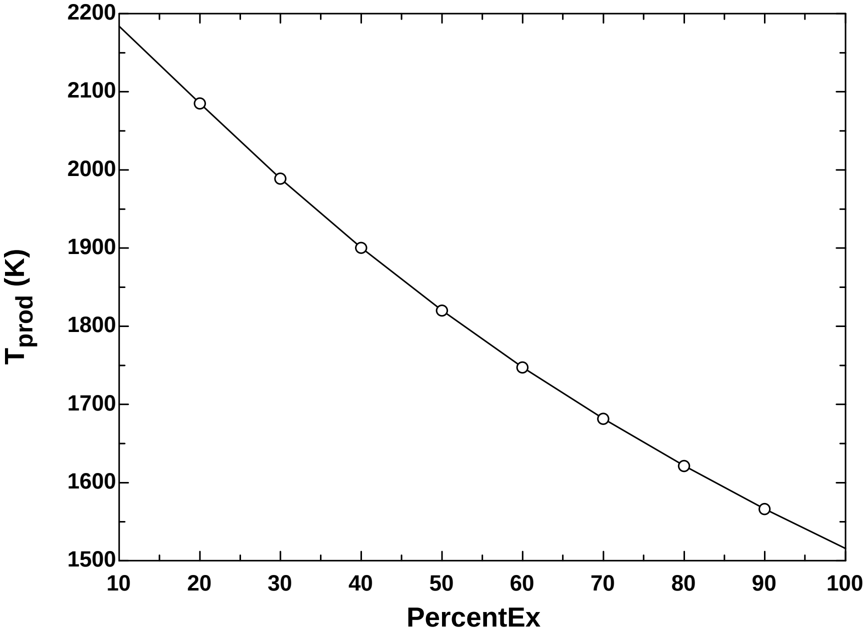
a_{th}	a	b	d	e	f	g	PercentEx [%]	T_{prod} [K]
3	1.922	0.07779	3	0.3081	12.38	0.0616	10	2184
3	1.971	0.0293	3	0.5798	13.5	0.06965	20	2085
3	1.988	0.01151	3	0.8713	14.63	0.06899	30	1989
3	1.995	0.004708	3	1.17	15.76	0.06426	40	1901
3	1.998	0.001993	3	1.472	16.89	0.05791	50	1820
3	1.999	0.0008688	3	1.775	18.02	0.05118	60	1747
3	2	0.0003884	3	2.078	19.15	0.04467	70	1682
3	2	0.0001774	3	2.381	20.28	0.03867	80	1621
3	2	0.00008262	3	2.683	21.42	0.0333	90	1566
3	2	0.00003914	3	2.986	22.55	0.02856	100	1516



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Variations of K_p with Temperature

16-55C It enables us to determine the enthalpy of reaction $\bar{h}_R$ from a knowledge of equilibrium constant K_P.

16-56C At 2000 K since combustion processes are exothermic, and exothermic reactions are more complete at lower temperatures.

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16-57 The $\overline{h}_R$ at a specified temperature is to be determined using the enthalpy and K_P data.

Assumptions Both the reactants and products are ideal gases.

Analysis (*a*) The complete combustion equation of CO can be expressed as

$$\mathrm{CO} + \tfrac{1}{2}\mathrm{O}_2 \Leftrightarrow \mathrm{CO}_2$$

The $\overline{h}_R$ of the combustion process of CO at 2200 K is the amount of energy released as one kmol of CO is burned in a steady-flow combustion chamber at a temperature of 2200 K, and can be determined from

$$\overline{h}_R = \sum N_P\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)_P - \sum N_R\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)_R$$

Assuming the CO, O_2 and CO_2 to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\overline{\mathbf{h}}_\mathbf{f}^\circ$ **kJ/kmol**	$\overline{\mathbf{h}}_{\mathbf{298\ K}}$ **kJ/kmol**	$\overline{\mathbf{h}}_{\mathbf{2200\ K}}$ **kJ/kmol**
CO_2	-393,520	9364	112,939
CO	-110,530	8669	72,688
O_2	0	8682	75,484

Substituting,

$$\begin{aligned}\overline{h}_R &= 1(-393{,}520 + 112{,}939 - 9364)\\ &\quad - 1(-110{,}530 + 72{,}688 - 8669)\\ &\quad - 0.5(0 + 75{,}484 - 8682)\\ &= \mathbf{-276{,}835\ kJ/kmol}\end{aligned}$$

(*b*) The $\overline{h}_R$ value at 2200 K can be estimated by using K_P values at 2000 K and 2400 K (the closest two temperatures to 2200 K for which K_P data are available) from Table A-28,

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

$$3.860 - 6.635 \cong \frac{\overline{h}_R}{8.314\ \mathrm{kJ/kmol \cdot K}}\left(\frac{1}{2000\ \mathrm{K}} - \frac{1}{2400\ \mathrm{K}}\right)$$

$$\overline{h}_R \cong \mathbf{-276{,}856\ \ kJ/kmol}$$

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16-58E The $\bar{h}_R$ at a specified temperature is to be determined using the enthalpy and K_P data.

Assumptions Both the reactants and products are ideal gases.

Analysis (*a*) The complete combustion equation of CO can be expressed as

$$CO + \tfrac{1}{2}O_2 \Leftrightarrow CO_2$$

The $\bar{h}_R$ of the combustion process of CO at 3960 R is the amount of energy released as one kmol of H_2 is burned in a steady-flow combustion chamber at a temperature of 3960 R, and can be determined from

$$\bar{h}_R = \sum N_P\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_P - \sum N_R\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_R$$

Assuming the CO, O_2 and CO_2 to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\bar{h}_f^\circ$ **Btu/lbmol**	$\bar{h}_{537\,R}$ **Btu/lbmol**	$\bar{h}_{3960\,R}$ **Btu/lbmol**
CO_2	-169,300	4027.5	48,647
CO	-47,540	3725.1	31,256.5
O_2	0	3725.1	32,440.5

Substituting,

$$\begin{aligned}\bar{h}_R &= 1(-169{,}300 + 48{,}647 - 4027.5)\\ &\quad - 1(-47{,}540 + 31{,}256.5 - 3725.1)\\ &\quad - 0.5(0 + 32{,}440.5 - 3725.1)\\ &= \mathbf{-119{,}030\ Btu/lbmol}\end{aligned}$$

(*b*) The $\bar{h}_R$ value at 3960 R can be estimated by using K_P values at 3600 R and 4320 R (the closest two temperatures to 3960 R for which K_P data are available) from Table A-28,

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

$$3.860 - 6.635 \cong \frac{\bar{h}_R}{1.986\ \text{Btu/lbmol}\cdot\text{R}}\left(\frac{1}{3600\ \text{R}} - \frac{1}{4320\ \text{R}}\right)$$

$$\bar{h}_R \cong \mathbf{-119{,}041\ \ Btu/lbmol}$$

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16-59 The K_P value of the combustion process $H_2 + 1/2O_2 \Leftrightarrow H_2O$ is to be determined at a specified temperature using $\bar{h}_R$ data and K_P value .

Assumptions Both the reactants and products are ideal gases.

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

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

The $\bar{h}_R$ of the specified reaction at 2400 K is the amount of energy released as one kmol of H_2 is burned in a steady-flow combustion chamber at a temperature of 2400 K, and can be determined from

$$\bar{h}_R = \sum N_P\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_P - \sum N_R\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_R$$

Assuming the H_2O, H_2 and O_2 to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\bar{h}_f^\circ$ **kJ/kmol**	$\bar{h}_{298\,K}$ **kJ/kmol**	$\bar{h}_{2400\,K}$ **kJ/kmol**
H_2O	-241,820	9904	103,508
H_2	0	8468	75,383
O_2	0	8682	83,174

Substituting,

$$\begin{aligned}\bar{h}_R &= 1(-241{,}820 + 103{,}508 - 9904)\\ &\quad - 1(0 + 75{,}383 - 8468)\\ &\quad - 0.5(0 + 83{,}174 - 8682)\\ &= -252{,}377\ \text{kJ/kmol}\end{aligned}$$

The K_P value at 2600 K can be estimated from the equation above by using this $\bar{h}_R$ value and the K_P value at 2200 K which is $\ln K_{P1} = 6.768$,

$$\ln K_{P2} - 6.768 \cong \frac{-252{,}377\ \text{kJ/kmol}}{8.314\ \text{kJ/kmol}\cdot\text{K}}\left(\frac{1}{2200\ \text{K}} - \frac{1}{2600\ \text{K}}\right)$$

$$\ln K_{P2} = 4.645 \qquad (\text{Table A-28: } \ln K_{P2} = 4.648)$$

or

$$K_{P2} = \mathbf{104.1}$$

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16-60 The $\bar{h}_R$ value for the dissociation process $CO_2 \Leftrightarrow CO + 1/2O_2$ 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 dissociation equation of CO_2 can be expressed as

$$CO_2 \Leftrightarrow CO + \tfrac{1}{2}O_2$$

The $\bar{h}_R$ of the dissociation process of CO_2 at 2200 K is the amount of energy absorbed or released as one kmol of CO_2 dissociates in a steady-flow combustion chamber at a temperature of 2200 K, and can be determined from

$$\bar{h}_R = \sum N_P\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_P - \sum N_R\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_R$$

Assuming the CO, O_2 and CO_2 to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\bar{\mathbf{h}}_{\mathbf{f}}^\circ$ **kJ/kmol**	$\bar{\mathbf{h}}_{\mathbf{298\,K}}$ **kJ/kmol**	$\bar{\mathbf{h}}_{\mathbf{2200\,K}}$ **kJ/kmol**
CO_2	-393,520	9364	112,939
CO	-110,530	8669	72,688
O_2	0	8682	75,484

Substituting,

$$\begin{aligned}\bar{h}_R &= 1(-110{,}530 + 72{,}688 - 8669)\\ &\quad + 0.5(0 + 75{,}484 - 8682)\\ &\quad - 1(-393{,}520 + 112{,}939 - 9364)\\ &= \mathbf{276{,}835\ kJ/kmol}\end{aligned}$$

(*b*) The $\bar{h}_R$ value at 2200 K can be estimated by using K_P values at 2000 K and 2400 K (the closest two temperatures to 2200 K for which K_P data are available) from Table A-28,

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

$$-3.860 - (-6.635) \cong \frac{\bar{h}_R}{8.314\ \text{kJ/kmol}\cdot\text{K}}\left(\frac{1}{2000\ \text{K}} - \frac{1}{2400\ \text{K}}\right)$$

$$\bar{h}_R \cong \mathbf{276{,}856\ kJ/kmol}$$

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16-61 The $\overline{h}_R$ value for the dissociation process $O_2 \Leftrightarrow 2O$ 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 dissociation equation of O_2 can be expressed as

$$O_2 \Leftrightarrow 2O$$

The $\overline{h}_R$ of the dissociation process of O_2 at 3100 K is the amount of energy absorbed or released as one kmol of O_2 dissociates in a steady-flow combustion chamber at a temperature of 3100 K, and can be determined from

$$\overline{h}_R = \sum N_P \left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)_P - \sum N_R \left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)_R$$

Assuming the O_2 and O to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\overline{\mathbf{h}}_\mathbf{f}^\circ$ kJ/kmol	$\overline{\mathbf{h}}_{\mathbf{298\ K}}$ kJ/kmol	$\overline{\mathbf{h}}_{\mathbf{2900\ K}}$ kJ/kmol
O	249,190	6852	65,520
O_2	0	8682	110,784

Substituting,

$$\begin{aligned}\overline{h}_R &= 2(249{,}190 + 65{,}520 - 6852) - 1(0 + 110{,}784 - 8682) \\ &= \mathbf{513{,}614\ kJ/kmol}\end{aligned}$$

(*b*) The $\overline{h}_R$ value at 3100 K can be estimated by using K_P values at 3000 K and 3200 K (the closest two temperatures to 3100 K for which K_P data are available) from Table A-28,

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

$$-3.072 - (-4.357) \cong \frac{\overline{h}_R}{8.314\ \text{kJ/kmol}\cdot\text{K}}\left(\frac{1}{3000\ \text{K}} - \frac{1}{3200\ \text{K}}\right)$$

$$\overline{h}_R \cong \mathbf{512{,}808\ \ kJ/kmol}$$

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16-62 The enthalpy of reaction for the equilibrium reaction CH4 + 2O2 = CO2 + 2H2O at 2500 K is to be estimated using enthalpy data and equilibrium constant, K_p data.

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

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

where

$$\Delta G^*(T) = \nu_{\mathrm{CO2}}\bar{g}^*_{\mathrm{CO2}}(T) + \nu_{\mathrm{H2O}}\bar{g}^*_{\mathrm{H2O}}(T) - \nu_{\mathrm{CH4}}\bar{g}^*_{\mathrm{CH4}}(T) - \nu_{\mathrm{O2}}\bar{g}^*_{\mathrm{O2}}(T)$$

At T_1 = 2500 - 10 = 2490 K:

$$\begin{aligned}\Delta G_1^*(T) &= \nu_{\mathrm{CO2}}\bar{g}^*_{\mathrm{CO2}}(T_1) + \nu_{\mathrm{H2O}}\bar{g}^*_{\mathrm{H2O}}(T_1) - \nu_{\mathrm{CH4}}\bar{g}^*_{\mathrm{CH4}}(T_1) - \nu_{\mathrm{O2}}\bar{g}^*_{\mathrm{O2}}(T_1)\\ &= 1(-1.075\times10^6) + 2(-830{,}577) - 1(-717{,}973) - 2(-611{,}582)\\ &= -794{,}929 \text{ kJ/kmol}\end{aligned}$$

At T_2 = 2500 + 10 = 2510 K:

$$\begin{aligned}\Delta G_2^*(T) &= \nu_{\mathrm{CO2}}\bar{g}^*_{\mathrm{CO2}}(T_2) + \nu_{\mathrm{H2O}}\bar{g}^*_{\mathrm{H2O}}(T_2) - \nu_{\mathrm{CH4}}\bar{g}^*_{\mathrm{CH4}}(T_2) - \nu_{\mathrm{O2}}\bar{g}^*_{\mathrm{O2}}(T_2)\\ &= 1(-1.081\times10^6) + 2(-836{,}100) - 1(-724{,}516) - 2(-617{,}124)\\ &= -794{,}801 \text{ kJ/kmol}\end{aligned}$$

The Gibbs functions are obtained from enthalpy and entropy properties using EES. Substituting,

$$K_{p1} = \exp\left(-\frac{-794{,}929 \text{ kJ/kmol}}{(8.314 \text{ kJ/kmol}\cdot\text{K})(2490 \text{ K})}\right) = 4.747\times10^{16}$$

$$K_{p2} = \exp\left(-\frac{-794{,}801 \text{ kJ/kmol}}{(8.314 \text{ kJ/kmol}\cdot\text{K})(2510 \text{ K})}\right) = 3.475\times10^{16}$$

The enthalpy of reaction is determined by using the integrated van't Hoff equation:

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

$$\ln\left(\frac{3.475\times10^{16}}{4.747\times10^{16}}\right) = \frac{\bar{h}_R}{8.314 \text{ kJ/kmol.K}}\left(\frac{1}{2490 \text{ K}} - \frac{1}{2510 \text{ K}}\right) \longrightarrow \bar{h}_R = \mathbf{-810{,}845\ kJ/kmol}$$

The enthalpy of reaction can also be determined from an energy balance to be

$$\bar{h}_R = H_P - H_R$$

where

$$H_R = 1\bar{h}_{\mathrm{CH4}\,@\,2500\,\mathrm{K}} + 2\bar{h}_{\mathrm{O2}\,@\,2500\,\mathrm{K}} = 96{,}668 + 2(78{,}377) = 253{,}422 \text{ kJ/kmol}$$

$$H_P = 1\bar{h}_{\mathrm{CO2}\,@\,2500\,\mathrm{K}} + 2\bar{h}_{\mathrm{H2O}\,@\,2500\,\mathrm{K}} = (-271{,}641) + 2(-142{,}891) = -557{,}423 \text{ kJ/kmol}$$

The enthalpies are obtained from EES. Substituting,

$$\bar{h}_R = H_P - H_R = (-557{,}423) - (253{,}422) = \mathbf{-810{,}845\ kJ/kmol}$$

which is identical to the value obtained using K_p data.

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Phase Equilibrium

16-63C No. Because the specific gibbs function of each phase will not be affected by this process; i.e., we will still have $g_f = g_g$.

16-64C Yes. Because the number of independent variables for a two-phase (PH=2), two-component (C=2) mixture is, from the phase rule,

$$\text{IV} = C - \text{PH} + 2 = 2 - 2 + 2 = 2$$

Therefore, two properties can be changed independently for this mixture. In other words, we can hold the temperature constant and vary the pressure and still be in the two-phase region. Notice that if we had a single component (C=1) two phase system, we would have IV=1, which means that fixing one independent property automatically fixes all the other properties.

11-65C Using solubility data of a solid in a specified liquid, the mass fraction w of the solid A in the liquid at the interface at a specified temperature can be determined from

$$\text{mf}_A = \frac{m_{\text{solid}}}{m_{\text{solid}} + m_{\text{liquid}}}$$

where m_{solid} is the maximum amount of solid dissolved in the liquid of mass m_{liquid} at the specified temperature.

11-66C The molar concentration C_{i} of the gas species i in the solid at the interface $C_{\text{i, solid side}}(0)$ is proportional to the *partial pressure* of the species i in the gas $P_{\text{i, gas side}}(0)$ on the gas side of the interface, and is determined from

$$C_{\text{i, solid side}}(0) = \text{S} \times P_{\text{i, gas side}}(0) \qquad (\text{kmol/m}^3)$$

where S is the *solubility* of the gas in that solid at the specified temperature.

11-67C Using Henry's constant data for a gas dissolved in a liquid, the mole fraction of the gas dissolved in the liquid at the interface at a specified temperature can be determined from Henry's law expressed as

$$y_{\text{i, liquid side}}(0) = \frac{P_{\text{i, gas side}}(0)}{H}$$

where H is *Henry's constant* and $P_{\text{i,gas side}}(0)$ is the partial pressure of the gas i at the gas side of the interface. This relation is applicable for dilute solutions (gases that are weakly soluble in liquids).

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16-68 It is to be shown that a mixture of saturated liquid water and saturated water vapor at 100°C satisfies the criterion for phase equilibrium.

Analysis Using the definition of Gibbs function and enthalpy and entropy data from Table A-4,

$$g_f = h_f - Ts_f = (419.17\ \text{kJ/kg}) - (373.15\ \text{K})(1.3072\ \text{kJ/kg}\cdot\text{K}) = -68.61\ \text{kJ/kg}$$
$$g_g = h_g - Ts_g = (2675.6\ \text{kJ/kg}) - (373.15\ \text{K})(7.3542\ \text{kJ/kg}\cdot\text{K}) = -68.62\ \text{kJ/kg}$$

which are practically same. Therefore, the criterion for phase equilibrium is satisfied.

16-69 It is to be shown that a mixture of saturated liquid water and saturated water vapor at 300 kPa satisfies the criterion for phase equilibrium.

Analysis The saturation temperature at 300 kPa is 406.7 K. Using the definition of Gibbs function and enthalpy and entropy data from Table A-5,

$$g_f = h_f - Ts_f = (561.43\ \text{kJ/kg}) - (406.7\ \text{K})(1.6717\ \text{kJ/kg}\cdot\text{K}) = -118.5\ \text{kJ/kg}$$
$$g_g = h_g - Ts_g = (2724.9\ \text{kJ/kg}) - (406.7\ \text{K})(6.9917\ \text{kJ/kg}\cdot\text{K}) = -118.6\ \text{kJ/kg}$$

which are practically same. Therefore, the criterion for phase equilibrium is satisfied.

16-70 It is to be shown that a saturated liquid-vapor mixture of refrigerant-134a at -10°C satisfies the criterion for phase equilibrium.

Analysis Using the definition of Gibbs function and enthalpy and entropy data from Table A-11,

$$g_f = h_f - Ts_f = (38.55\ \text{kJ/kg}) - (263.15\ \text{K})(0.15504\ \text{kJ/kg}\cdot\text{K}) = -2.249\ \text{kJ/kg}$$
$$g_g = h_g - Ts_g = (244.51\ \text{kJ/kg}) - (263.15\ \text{K})(0.93766\ \text{kJ/kg}\cdot\text{K}) = -2.235\ \text{kJ/kg}$$

which are sufficiently close. Therefore, the criterion for phase equilibrium is satisfied.

16-71 The number of independent properties needed to fix the state of a mixture of oxygen and nitrogen in the gas phase is to be determined.

Analysis In this case the number of components is $C = 2$ and the number of phases is PH = 1. Then the number of independent variables is determined from the phase rule to be

$$\text{IV} = C - \text{PH} + 2 = 2 - 1 + 2 = 3$$

Therefore, three independent properties need to be specified to fix the state. They can be temperature, the pressure, and the mole fraction of one of the gases.

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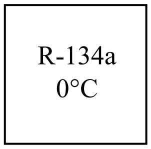
16-72 The values of the Gibbs function for saturated refrigerant-134a at 0°C as a saturated liquid, saturated vapor, and a mixture of liquid and vapor are to be calculated.

Analysis Obtaining properties from Table A-11, the Gibbs function for the liquid phase is,

$$g_f = h_f - Ts_f = 51.86\text{ kJ/kg} - (273.15\text{ K})(0.20439\text{ kJ/kg}\cdot\text{K}) = \mathbf{-3.97\text{ kJ/kg}}$$



For the vapor phase,

$$g_g = h_g - Ts_g = 250.45\text{ kJ/kg} - (273.15\text{ K})(0.93139\text{ kJ/kg}\cdot\text{K}) = \mathbf{-3.96\text{ kJ/kg}}$$

For the saturated mixture with a quality of 30%,

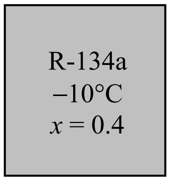
$$h = h_f + xh_{fg} = 51.86\text{ kJ/kg} + (0.30)(198.60\text{ kJ/kg}) = 111.44\text{ kJ/kg}$$
$$s = s_f + xs_{fg} = 0.20439\text{ kJ/kg}\cdot\text{K} + (0.30)(0.72701\text{ kJ/kg}\cdot\text{K}) = 0.42249\text{ kJ/kg}\cdot\text{K}$$
$$g = h - Ts = 111.44\text{ kJ/kg} - (273.15\text{ kJ/kg})(0.42249\text{ kJ/kg}\cdot\text{K}) = \mathbf{-3.96\text{ kJ/kg}}$$

The results agree and demonstrate that phase equilibrium exists.

16-73 The values of the Gibbs function for saturated refrigerant-134a at -10°C are to be calculated.

Analysis Obtaining properties from Table A-11, the Gibbs function for the liquid phase is,

$$g_f = h_f - Ts_f = 38.55\text{ kJ/kg} - (263.15\text{ K})(0.15504\text{ kJ/kg}\cdot\text{K}) = \mathbf{-2.25\text{ kJ/kg}}$$



For the vapor phase,

$$g_g = h_g - Ts_g = 244.51\text{ kJ/kg} - (263.15\text{ K})(0.93766\text{ kJ/kg}\cdot\text{K}) = \mathbf{-2.24\text{ kJ/kg}}$$

The results agree and demonstrate that phase equilibrium exists.

16-74 Using the liquid-vapor equilibrium diagram of an oxygen-nitrogen mixture at a specified pressure, the temperature is to be determined for a specified composition of the nitrogen and the mass fraction of the oxygen at this temperature is to be determined.

Analysis From the equilibrium diagram (Fig. 16-21) we read $T = \mathbf{88\text{ K}}$.

For the liquid phase, from the same figure,

$$y_{f,\text{O2}} = 0.90 \quad \text{and} \quad y_{f,\text{N2}} = 0.10$$

Then,

$$\text{mf}_{f,\text{O2}} = \frac{m_{f,\text{O2}}}{m_{f,\text{total}}} = \frac{y_{f,\text{O2}}M_{\text{O2}}}{y_{f,\text{O2}}M_{\text{O2}} + y_{f,\text{N2}}M_{\text{N2}}} = \frac{(0.90)(32)}{(0.90)(32) + (0.10)(28)} = \mathbf{0.911}$$

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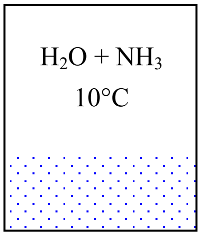
16-75 A liquid-vapor mixture of ammonia and water in equilibrium at a specified temperature is considered. The pressure of ammonia is to be determined for two compositions of the liquid phase.

Assumptions The mixture is ideal and thus Raoult's law is applicable.



Analysis According to Raoults's law, when the mole fraction of the ammonia liquid is 20%,

$$P_{\mathrm{NH3}} = y_{f,\mathrm{NH3}} P_{\mathrm{sat,NH3}}(T) = 0.20(615.3\ \mathrm{kPa}) = \mathbf{123.1\ kPa}$$

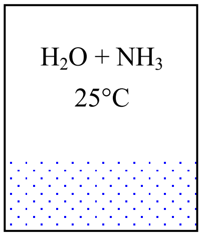
When the mole fraction of the ammonia liquid is 80%,

$$P_{\mathrm{NH3}} = y_{f,\mathrm{NH3}} P_{\mathrm{sat,NH3}}(T) = 0.80(615.3\ \mathrm{kPa}) = \mathbf{492.2\ kPa}$$

16-76 A liquid-vapor mixture of ammonia and water in equilibrium at a specified temperature is considered. The composition of the liquid phase is given. The composition of the vapor phase is to be determined.

Assumptions The mixture is ideal and thus Raoult's law is applicable.

Properties At 25°C, $P_{\mathrm{sat,H_2O}} = 3.170\ \mathrm{kPa}$ and $P_{\mathrm{sat,NH_3}} = 1003.5\ \mathrm{kPa}$.



Analysis The vapor pressures are

$$P_{\mathrm{H_2O}} = y_{f,\mathrm{H_2O}} P_{\mathrm{sat,H_2O}}(T) = 0.50(3.170\ \mathrm{kPa}) = 1.585\ \mathrm{kPa}$$
$$P_{\mathrm{NH_3}} = y_{f,\mathrm{NH_3}} P_{\mathrm{sat,NH_3}}(T) = 0.50(1003.5\ \mathrm{kPa}) = 501.74\ \mathrm{kPa}$$

Thus the total pressure of the mixture is

$$P_{\mathrm{total}} = P_{\mathrm{H_2O}} + P_{\mathrm{NH_3}} = (1.585 + 501.74)\ \mathrm{kPa} = 503.33\ \mathrm{kPa}$$

Then the mole fractions in the vapor phase become

$$y_{g,\mathrm{H_2O}} = \frac{P_{\mathrm{H_2O}}}{P_{\mathrm{total}}} = \frac{1.585\ \mathrm{kPa}}{503.33\ \mathrm{kPa}} = \mathbf{0.0031} \quad \text{or} \quad 0.31\%$$
$$y_{g,\mathrm{NH_3}} = \frac{P_{\mathrm{NH_3}}}{P_{\mathrm{total}}} = \frac{501.74\ \mathrm{kPa}}{503.33\ \mathrm{kPa}} = \mathbf{0.9969} \quad \text{or} \quad 99.69\%$$

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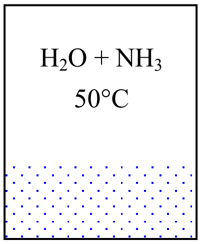
16-77 A liquid-vapor mixture of ammonia and water in equilibrium at a specified temperature is considered. The composition of the vapor phase is given. The composition of the liquid phase is to be determined.

Assumptions The mixture is ideal and thus Raoult's law is applicable.

Properties At 50°C, $P_{\text{sat},H_2O} = 12.352\text{ kPa}$ and $P_{\text{sat},NH_3} = 2033.5\text{ kPa}$.

Analysis We have $y_{g,H_2O} = 1\%$ and $y_{g,NH_3} = 99\%$. For an ideal two-phase mixture we have



$$y_{g,H_2O} P_m = y_{f,H_2O} P_{\text{sat},H_2O}(T)$$
$$y_{g,NH_3} P_m = y_{f,NH_3} P_{\text{sat},NH_3}(T)$$
$$y_{f,H_2O} + y_{f,NH_3} = 1$$

Solving for $y_{f,H_2O,}$

$$y_{f,H_2O} = \frac{y_{g,H_2O} P_{\text{sat},NH_3}}{y_{g,NH_3} P_{\text{sat},H_2O}}(1 - y_{f,H_2O}) = \frac{(0.01)(2033.5\text{ kPa})}{(0.99)(12.352\text{ kPa})}(1 - y_{f,H_2O})$$

It yields

$$y_{f,H_2O} = \mathbf{0.624} \quad \text{and} \quad y_{f,NH_3} = \mathbf{0.376}$$

16-78 Using the liquid-vapor equilibrium diagram of an oxygen-nitrogen mixture, the composition of each phase at a specified temperature and pressure is to be determined.

Analysis From the equilibrium diagram (Fig. 16-21) we read

Liquid: 30% N_2 and 70% O_2

Vapor: 66% N_2 and 34% O_2

16-79 Using the liquid-vapor equilibrium diagram of an oxygen-nitrogen mixture at a specified pressure, the temperature is to be determined for a specified composition of the vapor phase.

Analysis From the equilibrium diagram (Fig. 16-21) we read T = **82 K**.

16-80 Using the liquid-vapor equilibrium diagram of an oxygen-nitrogen mixture at a specified pressure, the temperature is to be determined for a specified composition of the liquid phase.

Analysis From the equilibrium diagram (Fig. 16-21) we read T = **84 K**.

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16-81 A rubber wall separates O_2 and N_2 gases. The molar concentrations of O_2 and N_2 in the wall are to be determined.

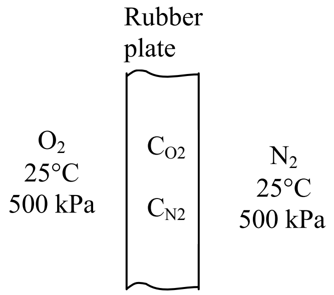
Assumptions The O_2 and N_2 gases are in phase equilibrium with the rubber wall.

Properties The molar mass of oxygen and nitrogen are 32.0 and 28.0 kg/kmol, respectively (Table A-1). The solubility of oxygen and nitrogen in rubber at 298 K are 0.00312 and 0.00156 kmol/m^3·bar, respectively (Table 16-3).

Analysis Noting that 500 kPa = 5 bar, the molar densities of oxygen and nitrogen in the rubber wall are determined to be

$$\begin{aligned} C_{O_2,\text{ solid side}}(0) &= S \times P_{O_2,\text{ gas side}} \\ &= (0.00312\text{ kmol/m}^3\text{.bar})(5\text{ bar}) \\ &= \mathbf{0.0156\ kmol/m^3} \end{aligned}$$

$$\begin{aligned} C_{N_2,\text{ solid side}}(0) &= S \times P_{N_2,\text{ gas side}} \\ &= (0.00156\text{ kmol / m}^3\text{.bar})(5\text{ bar}) \\ &= \mathbf{0.0078\ kmol / m^3} \end{aligned}$$



That is, there will be 0.0156 kmol of O_2 and 0.0078 kmol of N_2 gas in each m^3 volume of the rubber wall.

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16-82 An ammonia-water absorption refrigeration unit is considered. The operating pressures in the generator and absorber, and the mole fractions of the ammonia in the strong liquid mixture being pumped from the absorber and the weak liquid solution being drained from the generator are to be determined.

Assumptions The mixture is ideal and thus Raoult's law is applicable.

Properties At $0°\text{C}, P_{\text{sat,H2O}} = 0.6112\text{ kPa}$ and at $46°\text{C}, P_{\text{sat,H2O}} = 10.10\text{ kPa}$ (Table A-4). The saturation pressures of ammonia at the same temperatures are given to be 430.6 kPa and 1830.2 kPa, respectively.

Analysis According to Raoults's law, the partial pressures of ammonia and water are given by

$$
\begin{aligned}
P_{\text{g,NH3}} &= y_{f,\text{NH3}} P_{\text{sat,NH3}} \\
P_{\text{g,H2O}} &= y_{f,\text{H2O}} P_{\text{sat,H2O}} = (1 - y_{f,\text{NH3}}) P_{\text{sat,H2O}}
\end{aligned}
$$

Using Dalton's partial pressure model for ideal gas mixtures, the mole fraction of the ammonia in the vapor mixture is

$$
y_{g,\text{NH3}} = \frac{y_{f,\text{NH3}} P_{\text{sat,NH3}}}{y_{f,\text{NH3}} P_{\text{sat,NH3}} + (1 - y_{f,\text{NH3}} P_{\text{sat,H2O}})}
$$

$$
0.96 = \frac{430.6 y_{f,\text{NH3}}}{430.6 y_{f,\text{NH3}} + 0.6112(1 - y_{f,\text{NH3}})} \longrightarrow y_{f,\text{NH3}} = \mathbf{0.03294}
$$

Then,

$$
\begin{aligned}
P &= y_{f,\text{NH3}} P_{\text{sat,NH3}} + (1 - y_{f,\text{NH3}}) P_{\text{sat,H2O}} \\
&= (0.03294)(430.6) + (1 - 0.03294)(0.6112) = \mathbf{14.78\ kPa}
\end{aligned}
$$

Performing the similar calculations for the regenerator,

$$
0.96 = \frac{1830.2 y_{f,\text{NH3}}}{1830.2 y_{f,\text{NH3}} + 10.10(1 - y_{f,\text{NH3}})} \longrightarrow y_{f,\text{NH3}} = \mathbf{0.1170}
$$

$$
P = (0.1170)(1830.2) + (1 - 0.1170)(10.10) = \mathbf{223.1 kPa}
$$

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16-83 An ammonia-water absorption refrigeration unit is considered. The operating pressures in the generator and absorber, and the mole fractions of the ammonia in the strong liquid mixture being pumped from the absorber and the weak liquid solution being drained from the generator are to be determined.

Assumptions The mixture is ideal and thus Raoult's law is applicable.

Properties At 6°C, $P_{\text{sat,H2O}} = 0.9353\text{ kPa}$ and at 40°C, $P_{\text{sat,H2O}} = 7.3851\text{ kPa}$ (Table A-4 or EES). The saturation pressures of ammonia at the same temperatures are given to be 534.8 kPa and 1556.7 kPa, respectively.

Analysis According to Raoults's law, the partial pressures of ammonia and water are given by

$$P_{\text{g,NH3}} = y_{f,\text{NH3}} P_{\text{sat,NH3}}$$

$$P_{\text{g,H2O}} = y_{f,\text{H2O}} P_{\text{sat,H2O}} = (1 - y_{f,\text{NH3}}) P_{\text{sat,H2O}}$$

Using Dalton's partial pressure model for ideal gas mixtures, the mole fraction of the ammonia in the vapor mixture is

$$y_{g,\text{NH3}} = \frac{y_{f,\text{NH3}} P_{\text{sat,NH3}}}{y_{f,\text{NH3}} P_{\text{sat,NH3}} + (1 - y_{f,\text{NH3}} P_{\text{sat,H2O}})}$$

$$0.96 = \frac{534.8 y_{f,\text{NH3}}}{534.8 y_{f,\text{NH3}} + 0.9353(1 - y_{f,\text{NH3}})} \longrightarrow y_{f,\text{NH3}} = \mathbf{0.04028}$$

Then,

$$P = y_{f,\text{NH3}} P_{\text{sat,NH3}} + (1 - y_{f,\text{NH3}}) P_{\text{sat,H2O}}$$

$$= (0.04028)(534.8) + (1 - 0.04028)(0.9353) = \mathbf{22.44\ kPa}$$

Performing the similar calculations for the regenerator,

$$0.96 = \frac{1556.7 y_{f,\text{NH3}}}{1556.7 y_{f,\text{NH3}} + 7.3851(1 - y_{f,\text{NH3}})} \longrightarrow y_{f,\text{NH3}} = \mathbf{0.1022}$$

$$P = (0.1022)(1556.7) + (1 - 0.1022)(7.3851) = \mathbf{165.7\ kPa}$$

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16-84 A liquid mixture of water and R-134a is considered. The mole fraction of the water and R-134a vapor are to be determined.

Assumptions The mixture is ideal and thus Raoult's law is applicable.

Properties At 20°C, $P_{\text{sat,H2O}} = 2.3392\text{ kPa}$ and $P_{\text{sat,R}} = 572.07\text{ kPa}$ (Tables A-4, A-11). The molar masses of water and R-134a are 18.015 and 102.03 kg/kmol, respectively (Table A-1).

Analysis The mole fraction of the water in the liquid mixture is

$$
\begin{aligned}
y_{f,\text{H2O}} &= \frac{N_{f,\text{H2O}}}{N_{\text{total}}} = \frac{\text{mf}_{f,\text{H2O}}/M_{\text{H2O}}}{(\text{mf}_{f,\text{H2O}}/M_{\text{H2O}}) + (\text{mf}_{f,\text{R}}/M_{\text{R}})} \\
&= \frac{0.9/18.015}{(0.9/18.015) + (0.1/102.03)} = 0.9808
\end{aligned}
$$

H_2O + R-134a
20°C

According to Raoults's law, the partial pressures of R-134a and water in the vapor mixture are

$$P_{g,\text{R}} = y_{f,\text{R}} P_{\text{sat,R}} = (1 - 0.9808)(572.07\text{ kPa}) = 10.98\text{ kPa}$$

$$P_{g,\text{H2O}} = y_{f,\text{H2O}} P_{\text{sat,H2O}} = (0.9808)(2.3392\text{ kPa}) = 2.294\text{ kPa}$$

The total pressure of the vapor mixture is then

$$P_{\text{total}} = P_{g,\text{R}} + P_{g,\text{H2O}} = 10.98 + 2.294 = 13.274\text{ kPa}$$

Based on Dalton's partial pressure model for ideal gases, the mole fractions in the vapor phase are

$$y_{g,\text{H2O}} = \frac{P_{g,\text{H2O}}}{P_{\text{total}}} = \frac{2.294\text{ kPa}}{13.274\text{ kPa}} = \mathbf{0.1728}$$

$$y_{g,\text{R}} = \frac{P_{g,\text{R}}}{P_{\text{total}}} = \frac{10.98\text{ kPa}}{13.274\text{ kPa}} = \mathbf{0.8272}$$

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16-85E A mixture of water and R-134a is considered. The mole fractions of the R-134a in the liquid and vapor phases are to be determined.

Assumptions The mixture is ideal and thus Raoult's law is applicable.

Properties At 77°F, $P_{\text{sat,H2O}} = 0.4597\text{ psia}$ and $P_{\text{sat,R}} = 96.56\text{ psia}$ (Tables A-4E, A-11E or EES).

Analysis According to Raoults's law, the partial pressures of R-134a and water in the vapor phase are given by

H_2O + R-134a
14.7 psia, 77°F

$$P_{g,\text{R}} = y_{f,\text{R}} P_{\text{sat,R}} = \frac{N_{f,\text{R}}}{N_{f,\text{R}} + N_{f,\text{H2O}}}(96.56\text{ psia})$$

$$P_{g,\text{H2O}} = y_{f,\text{H2O}} P_{\text{sat,H2O}} = \frac{N_{f,\text{H2O}}}{N_{f,\text{H2O}} + N_{f,\text{H2O}}}(0.4597\text{ psia})$$

The sum of these two partial pressures must equal the total pressure of the vapor mixture. In terms of $x = \dfrac{N_{f,\text{H2O}}}{N_{f,\text{R}}}$, this sum is

$$\frac{96.56}{x+1} + \frac{0.4597x}{x+1} = 14.7$$

Solving this expression for x gives

$$x = 5.748\text{ kmol H2O/kmol R-134a}$$

In the vapor phase, the partial pressure of the R-134a vapor is

$$P_{g,\text{R}} = \frac{96.56}{x+1} = \frac{96.56}{5.748+1} = 14.31\text{ psia}$$

The mole fraction of R-134a in the vapor phase is then

$$y_{g,\text{R}} = \frac{P_{g,\text{R}}}{P} = \frac{14.31\text{ psia}}{14.7\text{ psia}} = \mathbf{0.9735}$$

According to Raoult's law,

$$y_{f,\text{R}} = \frac{P_{g,\text{R}}}{P_{\text{sat,R}}} = \frac{14.31\text{ psia}}{96.56\text{ psia}} = \mathbf{0.1482}$$

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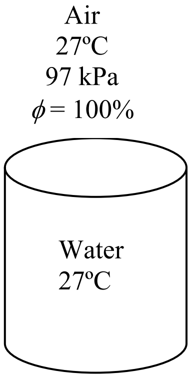
16-86 A glass of water is left in a room. The mole fraction of the water vapor in the air and the mole fraction of air in the water are to be determined when the water and the air are in thermal and phase equilibrium.

Assumptions **1** Both the air and water vapor are ideal gases. **2** Air is saturated since the humidity is 100 percent. **3** Air is weakly soluble in water and thus Henry's law is applicable.

Properties The saturation pressure of water at 27°C is 3.568 kPa (Table A-4). Henry's constant for air dissolved in water at 27ºC (300 K) is given in Table 16-2 to be H = 74,000 bar. Molar masses of dry air and water are 29 and 18 kg/kmol, respectively (Table A-1).

Analysis (*a*) Noting that air is saturated, the partial pressure of water vapor in the air will simply be the saturation pressure of water at 27°C,

$$P_{\text{vapor}} = P_{\text{sat @ 27°C}} = 3.600 \text{ kPa} \quad \text{(Table A-4)}$$



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

$$y_{\text{vapor}} = \frac{P_{\text{vapor}}}{P} = \frac{3.600 \text{ kPa}}{97 \text{ kPa}} = \mathbf{0.0371}$$

(*b*) Noting that the total pressure is 97 kPa, the partial pressure of dry air is

$$P_{\text{dry air}} = P - P_{\text{vapor}} = 97 - 3.600 = 93.4 \text{ kPa} = 0.934 \text{ bar}$$

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

$$y_{\text{dry air,liquid side}} = \frac{P_{\text{dry air,gas side}}}{H} = \frac{0.934 \text{ bar}}{74{,}000 \text{ bar}} = \mathbf{1.26 \times 10^{-5}}$$

Discussion The amount of air dissolved in water is very small, as expected.

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16-87 A carbonated drink in a bottle is considered. Assuming the gas space above the liquid consists of a saturated mixture of CO_2 and water vapor and treating the drink as a water, determine the mole fraction of the water vapor in the CO_2 gas and the mass of dissolved CO_2 in a 300 ml drink are to be determined when the water and the CO_2 gas are in thermal and phase equilibrium.

Assumptions **1** The liquid drink can be treated as water. **2** Both the CO_2 and the water vapor are ideal gases. **3** The CO_2 gas and water vapor in the bottle from a saturated mixture. **4** The CO_2 is weakly soluble in water and thus Henry's law is applicable.

Properties The saturation pressure of water at 27°C is 3.568 kPa (Table A-4). Henry's constant for CO_2 dissolved in water at 27ºC (300 K) is given in Table 16-2 to be $H = 1710$ bar. Molar masses of CO_2 and water are 44 and 18 kg/kmol, respectively (Table A-1).

Analysis (*a*) Noting that the CO_2 gas in the bottle is saturated, the partial pressure of water vapor in the air will simply be the saturation pressure of water at 27°C,

$$P_{\text{vapor}} = P_{\text{sat @ 27°C}} = 3.568 \text{ kPa} \quad \text{(more accurate EES value compared to interpolation value from Table A-4)}$$

Assuming both CO_2 and vapor to be ideal gases, the mole fraction of water vapor in the CO_2 gas becomes

$$y_{\text{vapor}} = \frac{P_{\text{vapor}}}{P} = \frac{3.568 \text{ kPa}}{130 \text{ kPa}} = \mathbf{0.0274}$$

(*b*) Noting that the total pressure is 130 kPa, the partial pressure of CO_2 is

$$P_{CO_2 \text{ gas}} = P - P_{\text{vapor}} = 130 - 3.568 = 126.4 \text{ kPa} = 1.264 \text{ bar}$$

From Henry's law, the mole fraction of CO_2 in the drink is determined to be

$$y_{CO_2\text{,liquid side}} = \frac{P_{CO_2\text{,gas side}}}{H} = \frac{1.264 \text{ bar}}{1710 \text{ bar}} = \mathbf{7.39 \times 10^{-4}}$$

Then the mole fraction of water in the drink becomes

$$y_{\text{water, liquid side}} = 1 - y_{CO_2\text{, liquid side}} = 1 - 7.39 \times 10^{-4} = 0.9993$$

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

$$\text{mf}_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m}$$

where the apparent molar mass of the drink (liquid water - CO_2 mixture) is

$$M_m = \sum y_i M_i = y_{\text{liquid water}} M_{\text{water}} + y_{CO_2} M_{CO_2} = 0.9993 \times 18.0 + (7.39 \times 10^{-4}) \times 44 = 18.02 \text{ kg / kmol}$$

Then the mass fraction of dissolved CO_2 gas in liquid water becomes

$$\text{mf}_{CO_2\text{, liquidside}} = y_{CO_2\text{, liquidside}} (0) \frac{M_{CO_2}}{M_m} = 7.39 \times 10^{-4} \frac{44}{18.02} = 0.00180$$

Therefore, the mass of dissolved CO_2 in a 300 ml ≈ 300 g drink is

$$m_{CO_2} = \text{mf}_{CO_2} m_m = (0.00180)(300 \text{ g}) = \mathbf{0.54 \text{ g}}$$

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Review Problems

16-88 The equilibrium constant of the dissociation process $O_2 \leftrightarrow 2O$ is given in Table A-28 at different temperatures. The value at a given temperature is to be verified using Gibbs function data.

Analysis The K_P value of a reaction at a specified temperature can be determined from the Gibbs function data using

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

$O_2 \leftrightarrow 2O$

2000 K

where

$$\begin{aligned}\Delta G^*(T) &= \nu_{\mathrm{O}}\bar{g}^*_{\mathrm{O}}(T) - \nu_{\mathrm{O_2}}\bar{g}^*_{\mathrm{O_2}}(T)\\ &= \nu_{\mathrm{O}}(\bar{h} - T\bar{s})_{\mathrm{O}} - \nu_{\mathrm{O_2}}(\bar{h} - T\bar{s})_{\mathrm{O_2}}\\ &= \nu_{\mathrm{O}}[(\bar{h}_f + \bar{h}_{2000} - \bar{h}_{298}) - T\bar{s}]_{\mathrm{O}} - \nu_{\mathrm{O_2}}[(\bar{h}_f + \bar{h}_{2000} - \bar{h}_{298}) - T\bar{s}]_{\mathrm{O_2}}\\ &= 2\times(249{,}190 + 42{,}564 - 6852 - 2000\times 201.135)\\ &\quad -1\times(0 + 67{,}881 - 8682 - 2000\times 268.655)\\ &= 243{,}375\ \text{kJ/kmol}\end{aligned}$$

Substituting,

$$\ln K_p = -(243{,}375\ \text{kJ/kmol})/[(8.314\ \text{kJ/kmol}\cdot\text{K})(2000\ \text{K})] = -14.636$$

or

$$K_p = \mathbf{4.4\times 10^{-7}} \qquad \text{(Table A-28: } \ln K_P = \text{-14.622)}$$

16-89 A mixture of H_2 and Ar is heated is heated until 15% of H_2 is dissociated. The final temperature of mixture is to be determined.

Assumptions **1** The constituents of the mixture are ideal gases. **2** Ar in the mixture remains an inert gas.

Analysis The stoichiometric and actual reactions can be written as

Stoichiometric: $\quad H_2 \Leftrightarrow 2H \quad (\text{thus } \nu_{H_2} = 1 \text{ and } \nu_H = 2)$

Actual: $\quad H_2 + Ar \longrightarrow \underbrace{0.3H}_{\text{prod}} + \underbrace{0.85H_2}_{\text{react.}} + \underbrace{Ar}_{\text{inert}}$

$H_2 \Leftrightarrow 2H$

Ar

1 atm

The equilibrium constant K_P can be determined from

$$K_p = \frac{N_H^{\nu_H}}{N_{H_2}^{\nu_{H_2}}}\left(\frac{P}{N_{\text{total}}}\right)^{\nu_H - \nu_{H_2}} = \frac{0.3^2}{0.85}\left(\frac{1}{0.85+0.3+1}\right)^{2-1} = 0.0492$$

From Table A-28, the temperature corresponding to this K_P value is T = **3117 K**.

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16-90 A mixture of H_2O, O_2, and N_2 is heated to a high temperature at a constant pressure. The equilibrium composition is to be determined.

Assumptions **1** The equilibrium composition consists of H_2O, O_2, N_2 and H_2. **2** The constituents of the mixture are ideal gases.

1 H_2O
2 O_2
5 N_2
2200 K
5 atm

Analysis The stoichiometric and actual reactions in this case are

Stoichiometric: $\mathrm{H_2O} \Leftrightarrow \mathrm{H_2} + \tfrac{1}{2}\mathrm{O_2}$ (thus $\nu_{\mathrm{H_2O}} = 1, \nu_{\mathrm{H_2}} = 1,$ and $\nu_{\mathrm{O_2}} = \tfrac{1}{2}$)

Actual: $\mathrm{H_2O} + 2\mathrm{O_2} + 5\mathrm{N_2} \longrightarrow \underbrace{x\mathrm{H_2O}}_{\text{react.}} + \underbrace{y\mathrm{H_2} + z\mathrm{O_2}}_{\text{products}} + \underbrace{5\mathrm{N_2}}_{\text{inert}}$

H balance: $2 = 2x + 2y \longrightarrow y = 1 - x$

O balance: $5 = x + 2z \longrightarrow z = 2.5 - 0.5x$

Total number of moles: $N_{\text{total}} = x + y + z + 5 = 8.5 - 0.5x$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{\mathrm{H_2}}^{\nu_{\mathrm{H_2}}} N_{\mathrm{O_2}}^{\nu_{\mathrm{O_2}}}}{N_{\mathrm{H_2O}}^{\nu_{\mathrm{H_2O}}}} \left(\frac{P}{N_{\text{total}}} \right)^{(\nu_{\mathrm{H_2}} - \nu_{\mathrm{O_2}} - \nu_{\mathrm{H_2O}})} = \frac{y \qquad z^{0.5}}{x} \left(\frac{P}{N_{\text{total}}} \right)^{1+0.5-1}$$

From Table A-28, lnK_P = -6.768 at 2200 K. Thus K_P = 0.00115. Substituting,

$$0.00115 = \frac{(1-x)(1.5-0.5x)^{0.5}}{x} \left(\frac{5}{8.5-0.5x} \right)^{0.5}$$

Solving for x,

$$x = 0.9981$$

Then,

$$y = 1 - x = 0.0019$$

$$z = 2.5 - 0.5x = 2.00095$$

Therefore, the equilibrium composition of the mixture at 2200 K and 5 atm is

$$\mathbf{0.9981H_2O + 0.0019H_2 + 2.00095O_2 + 5N_2}$$

The equilibrium constant for the reaction $\mathrm{H_2O} \Leftrightarrow \mathrm{OH} + \tfrac{1}{2}\mathrm{H_2}$ is lnK_P = -7.148, 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.

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16-91 [*Also solved by EES on enclosed CD*] Methane gas is burned with stoichiometric amount of air during a combustion process. The equilibrium composition and the exit temperature are to be determined.

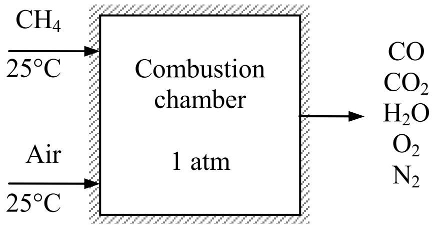
Assumptions **1** The product gases consist of CO_2, H_2O, CO, N_2, and O_2. **2** The constituents of the mixture are ideal gases. **3** This is an adiabatic and steady-flow combustion process.

Analysis (*a*) The combustion equation of CH_4 with stoichiometric amount of O_2 can be written as

$$CH_4 + 2(O_2 + 3.76N_2) \longrightarrow xCO_2 + (1-x)CO + (0.5-0.5x)O_2 + 2H_2O + 7.52N_2$$

After combustion, there will be no CH_4 present in the combustion chamber, and H_2O will act like an inert gas. The equilibrium equation among CO_2, CO, and O_2 can be expressed as

$$CO_2 \Leftrightarrow CO + \tfrac{1}{2}O_2 \quad (\text{thus } \nu_{CO_2} = 1,\ \nu_{CO} = 1,\ \text{and } \nu_{O_2} = \tfrac{1}{2})$$



and

$$K_p = \frac{N_{CO}^{\nu_{CO}} N_{O_2}^{\nu_{O_2}}}{N_{CO_2}^{\nu_{CO_2}}} \left(\frac{P}{N_{total}}\right)^{(\nu_{CO}+\nu_{O_2}-\nu_{CO_2})}$$

where

$$N_{total} = x + (1-x) + (1.5-0.5x) + 2 + 7.52 = 12.02 - 0.5x$$

Substituting,

$$K_p = \frac{(1-x)(0.5-0.5x)^{0.5}}{x}\left(\frac{1}{12.02-0.5x}\right)^{1.5-1}$$

The value of K_P depends on temperature of the products, which is yet to be determined. A second relation to determine K_P and x is obtained from the steady-flow energy balance expressed as

$$0 = \sum N_P\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_P - \sum N_R\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_R \longrightarrow 0 = \sum N_P\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_P - \sum N_R \bar{h}_{f\,R}^\circ$$

since the combustion is adiabatic and the reactants enter the combustion chamber at 25°C. Assuming the air and the combustion products to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\bar{\mathbf{h}}_f^\circ$ **kJ/kmol**	$\bar{\mathbf{h}}_{298\,K}$ **kJ/kmol**
$CH_4(g)$	-74,850	--
N_2	0	8669
O_2	0	8682
$H_2O(g)$	-241,820	9904
CO	-110,530	8669
CO_2	-393,520	9364

Substituting,

$$\begin{aligned}0 &= x(-393{,}520 + \bar{h}_{CO_2} - 9364) + (1-x)(-110{,}530 + \bar{h}_{CO} - 8669)\\&\quad + 2(-241{,}820 + \bar{h}_{H_2O} - 9904) + (0.5-0.5x)(0 + \bar{h}_{O_2} - 8682)\\&\quad + 7.52(0 + \bar{h}_{N_2} - 8669) - 1(-74{,}850 + h_{298} - h_{298}) - 0 - 0\end{aligned}$$

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which yields

$$x\bar{h}_{CO_2} + (1-x)\bar{h}_{CO} + 2\bar{h}_{H_2O} + (0.5-0.5x)\bar{h}_{O_2} + 7.52\bar{h}_{N_2} - 279{,}344x = 617{,}329$$

Now we have two equations with two unknowns, T_P and x. The solution is obtained by trial and error by assuming a temperature T_P, calculating the equilibrium composition from the first equation, and then checking to see if the second equation is satisfied. A first guess is obtained by assuming there is no CO in the products, i.e., x = 1. It yields T_P = 2328 K. The adiabatic combustion temperature with incomplete combustion will be less.

$$\text{Take } T_p = 2300\text{ K} \longrightarrow \ln K_p = -4.49 \longrightarrow x = 0.870 \longrightarrow RHS = 641{,}093$$

$$\text{Take } T_p = 2250\text{ K} \longrightarrow \ln K_p = -4.805 \longrightarrow x = 0.893 \longrightarrow RHS = 612{,}755$$

By interpolation,

$$T_p = \mathbf{2258\ K} \quad \text{and} \quad x = 0.889$$

Thus the composition of the equilibrium mixture is

$$\mathbf{0.889CO_2 + 0.111CO + 0.0555O_2 + 2H_2O + 7.52N_2}$$

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16-92 EES Problem 16-91 is reconsidered. The effect of excess air on the equilibrium composition and the exit temperature by varying the percent excess air from 0 to 200 percent is to be studied.

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

```
"Often, for nonlinear problems such as this one, good gusses are required to start the solution.
First, run the program with zero percent excess air to determine the net heat transfer as a function
of T_prod.  Just press F3 or click on the Solve Table icon.  From Plot Window 1, where Q_net is
plotted vs T_prod, determnine the value of T_prod for Q_net=0 by holding down the Shift key and
move the cross hairs by moving the mouse.  Q_net is approximately zero at T_prod = 2269 K.
From Plot Window 2 at T_prod = 2269 K, a, b, and c are approximately 0.89, 0.10, and 0.056,
respectively." "For EES to calculate a, b, c, and T_prod directly for the adiabatic case, remove the
'{ }' in the last line of this window to set Q_net = 0.0.  Then from the Options menu select  Variable
Info and set the Guess Values of a, b, c, and T_prod to the guess values selected from the Plot
Windows. Then press F2 or click on the Calculator icon."

"Input Data"
{PercentEx = 0}
Ex = PercentEX/100
P_prod =101.3 [kPa]
R_u=8.314 [kJ/kmol-K]
T_fuel=298 [K]
T_air=298 [K]
"The combustion equation of CH4 with stoichiometric amount of air is
CH4 + (1+Ex)(2)(O2 + 3.76N2)=CO2 +2H2O+(1+Ex)(2)(3.76)N2"
"For the incomplete combustion process in this problem, the combustion equation is
CH4 + (1+Ex)(2)(O2 + 3.76N2)=aCO2 +bCO + cO2+2H2O+(1+Ex)(2)(3.76)N2"
"Specie balance equations"
"O"
4=a *2+b +c *2+2
"C"
1=a +b
N_tot =a +b +c +2+(1+Ex)*(2)*3.76   "Total kilomoles of products at equilibrium"
"We assume the equilibrium reaction is
CO2=CO+0.5O2"
"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)
 "The standard-state Gibbs function is"
DELTAG =1*g_CO+0.5*g_O2-1*g_CO2
"The equilibrium constant is given by Eq. 16-14."
K_P  = exp(-DELTAG /(R_u*T_prod ))
P=P_prod /101.3"atm"
"The equilibrium constant is also given by Eq. 16-15."
"K_ P = (P/N_tot)^(1+0.5-1)*(b^1*c^0.5)/(a^1)"
sqrt(P/N_tot )*b *sqrt(c )=K_P *a
"Conservation of energy for the reaction, assuming SSSF, neglecting work ,  ke, and pe:"
E_in - E_out = DELTAE_cv
E_in = Q_net + HR
"The enthalpy of the reactant gases is"
HR=enthalpy(CH4,T=T_fuel)+ (1+Ex)*(2) *enthalpy(O2,T=T_air)+(1+Ex)*(2)*3.76
*enthalpy(N2,T=T_air)
E_out = HP
"The enthalpy of the product gases is"
```

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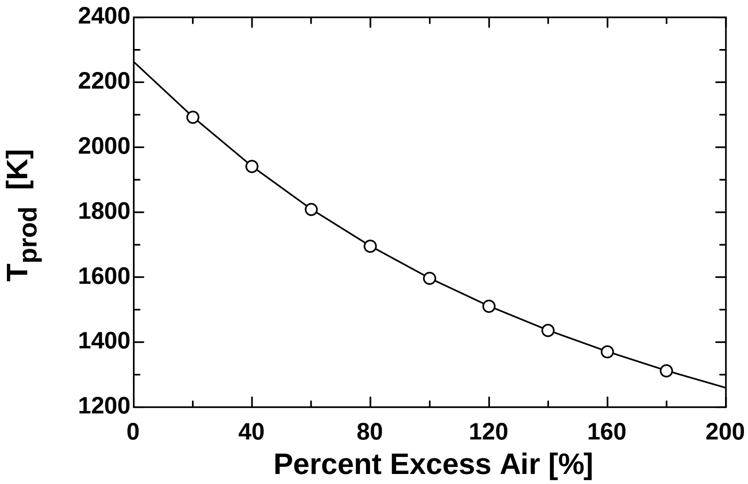
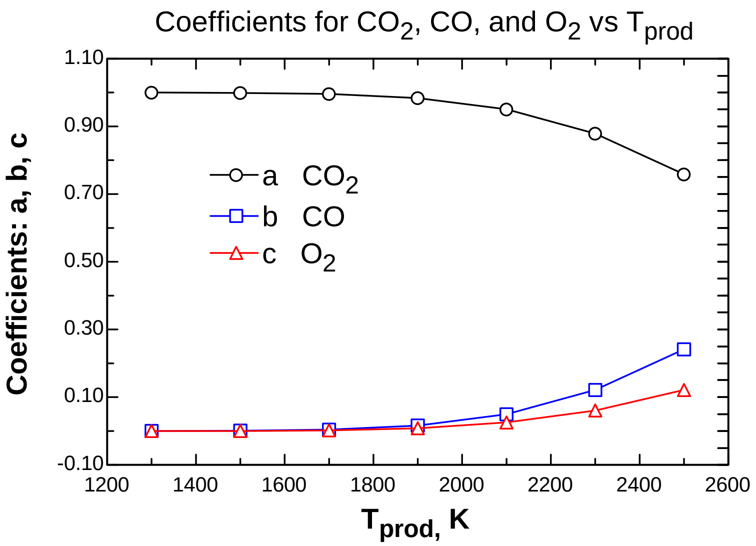
HP=a *enthalpy(CO2,T=T_prod )+b *enthalpy(CO,T=T_prod ) +2*enthalpy(H2O,T=T_prod
)+(1+Ex)*(2)*3.76*enthalpy(N2,T=T_prod ) + c *enthalpy(O2,T=T_prod )
DELTAE_cv = 0  "Steady-flow requirement"
Q_net=0 "For an adiabatic reaction the net heat added is zero."
```

PercentEx	T_{prod} [K]
0	2260
20	2091
40	1940
60	1809
80	1695
100	1597
120	1511
140	1437
160	1370
180	1312
200	1259





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16-93 The equilibrium constant for the reaction $CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O$ at 100 kPa and 2000 K is to be determined.

Assumptions **1** The constituents of the mixture are ideal gases.

Analysis This is a simultaneous reaction. We can begin with the dissociation of methane and carbon dioxide,

$$\mathrm{CH_4 \Leftrightarrow C + 2H_2} \qquad K_P = e^{-7.847}$$

$$\mathrm{C + O_2 \Leftrightarrow CO_2} \qquad K_P = e^{23.839}$$

When these two reactions are summed and the common carbon term cancelled, the result is

$$\mathrm{CH_4 + O_2 \Leftrightarrow CO_2 + 2H_2} \qquad K_P = e^{(23.839-7.847)} = e^{15.992}$$

$CH_4+2O_2 \Leftrightarrow$
CO_2+2H_2O
2000 K
100 kPa

Next, we include the water dissociation reaction (Table A-28),

$$\mathrm{2H_2 + O_2 \Leftrightarrow 2H_2O} \qquad K_P = e^{2(8.145)} = e^{16.29}$$

which when summed with the previous reaction and the common hydrogen term is cancelled yields

$$\mathrm{CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O} \qquad K_P = e^{15.992+16.29} = e^{32.282}$$

Then,

$$\ln K_P = \mathbf{32.282}$$

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16-94 The equilibrium mole fraction of the water vapor for the reaction $CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O$ at 100 kPa and 2000 K is to be determined.

Assumptions **1** The equilibrium composition consists of CH_4, O_2, CO_2, and H_2O. **2** The constituents of the mixture are ideal gases.

Analysis This is a simultaneous reaction. We can begin with the dissociation of methane and carbon dioxide,

$$\mathrm{CH_4} \Leftrightarrow \mathrm{C} + 2\mathrm{H_2} \qquad K_P = e^{-7.847}$$

$$\mathrm{C} + \mathrm{O_2} \Leftrightarrow \mathrm{CO_2} \qquad K_P = e^{23.839}$$

When these two reactions are summed and the common carbon term cancelled, the result is

$$\mathrm{CH_4} + \mathrm{O_2} \Leftrightarrow \mathrm{CO_2} + 2\mathrm{H_2} \qquad K_P = e^{(23.839-7.847)} = e^{15.992}$$

$CH_4+2O_2 \Leftrightarrow$
CO_2+2H_2O
2000 K
100 kPa

Next, we include the water dissociation reaction,

$$2\mathrm{H_2} + \mathrm{O_2} \Leftrightarrow 2\mathrm{H_2O} \qquad K_P = e^{2(8.145)} = e^{16.29}$$

which when summed with the previous reaction and the common hydrogen term is cancelled yields

$$\mathrm{CH_4} + 2\mathrm{O_2} \Leftrightarrow \mathrm{CO_2} + 2\mathrm{H_2O} \qquad K_P = e^{15.992+16.29} = e^{32.282}$$

Then,

$$\ln K_P = 32.282$$

Actual reeaction: $\mathrm{CH_4} + 2\mathrm{O_2} \longrightarrow \underbrace{x\mathrm{CH_4} + y\mathrm{O_2}}_{\text{react.}} + \underbrace{z\mathrm{CO_2} + m\mathrm{H_2O}}_{\text{products}}$

C balance: $1 = x + z \longrightarrow z = 1 - x$

H balance: $4 = 4x + 2m \longrightarrow m = 2 - 2x$

O balance: $4 = 2y + 2z + m \longrightarrow y = 2x$

Total number of moles: $N_{\text{total}} = x + y + z + m = 3$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{\mathrm{CO2}}^{\nu_{\mathrm{CO2}}} N_{\mathrm{H2O}}^{\nu_{\mathrm{H2O}}}}{N_{\mathrm{CH4}}^{\nu_{\mathrm{CH4}}} N_{\mathrm{O2}}^{\nu_{\mathrm{O2}}}} \left(\frac{P}{N_{\text{total}}}\right)^{\nu_{\mathrm{CO2}}+\nu_{\mathrm{H2O}}-\nu_{\mathrm{CH4}}-\nu_{\mathrm{O2}}}$$

Substituting,

$$e^{32.282} = \frac{(1-x)(2-2x)^2}{x(2x)^2} \left(\frac{100/101.325}{3}\right)^{1+2-1-2}$$

Solving for x,

$$x = 0.00002122$$

Then,

$$y = 2x = 0.00004244$$

$$z = 1 - x = 0.99997878$$

$$m = 2 - 2x = 1.99995756$$

Therefore, the equilibrium composition of the mixture at 2000 K and 100 kPa is

$$0.00002122\,\mathrm{CH_4} + 0.00004244\,\mathrm{O_2} + 0.99997878\,\mathrm{CO_2} + 1.99995756\,\mathrm{H_2O}$$

The mole fraction of water vapor is then

$$y_{\mathrm{H2O}} = \frac{1.99995756}{3} = \mathbf{0.6667}$$

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16-95 The equilibrium partial pressure of the carbon dioxide for the reaction $CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O$ at 700 kPa and 3000 K is to be determined.

Assumptions **1** The equilibrium composition consists of CH_4, O_2, CO_2, and H_2O. **2** The constituents of the mixture are ideal gases.

Analysis This is a simultaneous reaction. We can begin with the dissociation of methane and carbon dioxide,

$CH_4+2O_2 \Leftrightarrow$
CO_2+2H_2O
3000 K
700 kPa

$$\mathrm{CH_4} \Leftrightarrow \mathrm{C} + 2\mathrm{H_2} \qquad K_P = e^{-9.685}$$

$$\mathrm{C} + \mathrm{O_2} \Leftrightarrow \mathrm{CO_2} \qquad K_P = e^{15.869}$$

When these two reactions are summed and the common carbon term cancelled, the result is

$$\mathrm{CH_4} + \mathrm{O_2} \Leftrightarrow \mathrm{CO_2} + 2\mathrm{H_2} \qquad K_P = e^{(15.869-9.685)} = e^{6.184}$$

Next, we include the water dissociation reaction,

$$2\mathrm{H_2} + \mathrm{O_2} \Leftrightarrow 2\mathrm{H_2O} \qquad K_P = e^{2(3.086)} = e^{6.172}$$

which when summed with the previous reaction and the common hydrogen term is cancelled yields

$$\mathrm{CH_4} + 2\mathrm{O_2} \Leftrightarrow \mathrm{CO_2} + 2\mathrm{H_2O} \qquad K_P = e^{6.184+6.172} = e^{12.356}$$

Then,

$$\ln K_P = 12.356$$

Actual reeaction: $\mathrm{CH_4} + 2\mathrm{O_2} \longrightarrow \underbrace{x\mathrm{CH_4} + y\mathrm{O_2}}_{\text{react.}} + \underbrace{z\mathrm{CO_2} + m\mathrm{H_2O}}_{\text{products}}$

C balance: $1 = x + z \longrightarrow z = 1 - x$

H balance: $4 = 4x + 2m \longrightarrow m = 2 - 2x$

O balance: $4 = 2y + 2z + m \longrightarrow y = 2x$

Total number of moles: $N_{\text{total}} = x + y + z + m = 3$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{\mathrm{CO2}}^{\nu_{\mathrm{CO2}}} N_{\mathrm{H2O}}^{\nu_{\mathrm{H2O}}}}{N_{\mathrm{CH4}}^{\nu_{\mathrm{CH4}}} N_{\mathrm{O2}}^{\nu_{\mathrm{O2}}}} \left(\frac{P}{N_{\text{total}}} \right)^{\nu_{\mathrm{CO2}} + \nu_{\mathrm{H2O}} - \nu_{\mathrm{CH4}} - \nu_{\mathrm{O2}}}$$

Substituting,

$$e^{12.356} = \frac{(1-x)(2-2x)^2}{x(2x)^2} \left(\frac{700/101.325}{3} \right)^{1+2-1-2}$$

Solving for x,

$$x = 0.01601$$

Then,

$y = 2x = 0.03202$

$z = 1 - x = 0.98399$

$m = 2 - 2x = 1.96798$

Therefore, the equilibrium composition of the mixture at 3000 K and 700 kPa is

$$0.01601\,\mathrm{CH_4} + 0.03202\,\mathrm{O_2} + 0.98399\,\mathrm{CO_2} + 1.96798\,\mathrm{H_2O}$$

The mole fraction of carbon dioxide is

$$y_{\mathrm{CO2}} = \frac{0.98399}{3} = 0.3280$$

and the partial pressure of the carbon dioxide in the product mixture is

$$P_{\mathrm{CO2}} = y_{\mathrm{CO2}} P = (0.3280)(700\ \mathrm{kPa}) = \mathbf{230\ kPa}$$

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16-96 Methane is heated from a specified state to another state. The amount of heat required is to be determined without and with dissociation cases.

Properties The molar mass and gas constant of methane are 16.043 kg/kmol and 0.5182 kJ/kg·K (Table A-1).

Assumptions **1** The equilibrium composition consists of O_2 and O. **2** The constituents of the mixture are ideal gases.

Analysis (*a*) An energy balance for the process gives

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\substack{\text{Net energy transfer}\\ \text{by heat, work, and mass}}} = \underbrace{\Delta E_{\text{system}}}_{\substack{\text{Change in internal, kinetic,}\\ \text{potential, etc. energies}}}$$

$$\begin{aligned} Q_{\text{in}} &= N(\bar{u}_2 - \bar{u}_1) \\ &= N\left[\bar{h}_2 - \bar{h}_1 - R_u(T_2 - T_1)\right] \end{aligned}$$

Using the empirical coefficients of Table A-2c,

$$\begin{aligned} \bar{h}_2 - \bar{h}_1 &= \int_1^2 c_p\,dT = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) + \frac{d}{4}(T_2^4 - T_1^4) \\ &= 19.89(1000 - 298) + \frac{0.05024}{2}(1000^2 - 298^2) + \frac{1.269\times 10^{-5}}{3}(1000^3 - 298^3) \\ &\quad + \frac{-11.01\times 10^{-9}}{4}(1000^4 - 298^4) \\ &= 38{,}239 \text{ kJ/kmol} \end{aligned}$$

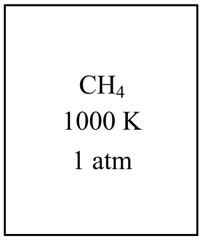
Substituting,

$$Q_{\text{in}} = (10 \text{ kmol})\left[38{,}239 \text{ kJ/kmol} - (8.314 \text{ kJ/kmol}\cdot\text{K})(1000 - 298)\text{K}\right] = \mathbf{324{,}000\ kJ}$$

(*b*) The stoichiometric and actual reactions in this case are

Stoichiometric: $CH_4 \Leftrightarrow C + 2H_2$ (thus $\nu_{CH4} = 1$, $\nu_C = 1$ and $\nu_{H2} = 2$)

Actual: $CH_4 \longrightarrow \underbrace{xCH_4}_{\text{react.}} + \underbrace{yC + zH_2}_{\text{products}}$



C balance: $1 = x + y \longrightarrow y = 1 - x$

H balance: $4 = 4x + 2z \longrightarrow z = 2 - 2x$

Total number of moles: $N_{\text{total}} = x + y + z = 3 - 2x$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_C^{\nu_C} N_{H2}^{\nu_{H2}}}{N_{CH4}^{\nu_{CH4}}}\left(\frac{P}{N_{\text{total}}}\right)^{\nu_C + \nu_{H2} - \nu_{CH4}}$$

From the problem statement, at 1000 K, $\ln K_p = -2.328$. Then,

$$K_P = e^{-2.328} = 0.09749$$

Substituting,

$$0.09749 = \frac{(1-x)(2-2x)^2}{x}\left(\frac{1}{3-2x}\right)^{1+2-1}$$

Solving for x,

$$x = 0.6414$$

Then,

$$y = 1 - x = 0.3586$$

$$z = 2 - 2x = 0.7172$$

Therefore, the equilibrium composition of the mixture at 1000 K and 1 atm is

$$0.6414\,\text{CH}_4 + 0.3586\,\text{C} + 0.7172\,\text{H}_2$$

The mole fractions are

$$y_{\text{CH4}} = \frac{N_{\text{CH4}}}{N_{\text{total}}} = \frac{0.6414}{0.6414 + 0.3586 + 0.7172} = \frac{0.6414}{1.7172} = 0.3735$$

$$y_{\text{C}} = \frac{N_{\text{C}}}{N_{\text{total}}} = \frac{0.3586}{1.7172} = 0.2088$$

$$y_{\text{H2}} = \frac{N_{\text{H2}}}{N_{\text{total}}} = \frac{0.7172}{1.7172} = 0.4177$$

The heat transfer can be determined from

$$\begin{aligned} Q_{\text{in}} &= N(y_{\text{CH4}}c_{v,\text{CH4}}T_2 + y_{\text{H2}}c_{v,\text{H2}}T_2 + y_{\text{C}}c_{v,\text{C}}T_2) - Nc_{v,\text{CH4}}T_1 \\ &= (10)\big[(0.3735)(63.3)(1000) + (0.4177)(21.7)(1000) + (0.2088)(0.711)(1000)\big] - (10)(27.8)(298) \\ &= \mathbf{245{,}700\ kJ} \end{aligned}$$

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16-97 Solid carbon is burned with a stoichiometric amount of air. The number of moles of CO_2 formed per mole of carbon is to be determined.

Assumptions **1** The equilibrium composition consists of CO_2, CO, O_2, and N_2. **2** The constituents of the mixture are ideal gases.

Analysis Inspection of Table A-28 reveals that the dissociation equilibrium constants of CO_2, O_2, and N_2 are quite small and therefore may be neglected. (We learned from another source that the equilibrium constant for CO is also small). The combustion is then complete and the reaction is described by

Carbon + Air
25°C

$$\mathrm{C} + (\mathrm{O}_2 + 3.76\mathrm{N}_2) \longrightarrow \mathrm{CO}_2 + 3.76\mathrm{N}_2$$

The number of moles of CO_2 in the products is then

$$\frac{N_{\mathrm{CO2}}}{N_{\mathrm{C}}} = \mathbf{1}$$

16-98 Solid carbon is burned with a stoichiometric amount of air. The amount of heat released per kilogram of carbon is to be determined.

Assumptions **1** The equilibrium composition consists of CO_2, CO, O_2, and N_2. **2** The constituents of the mixture are ideal gases.

Analysis Inspection of Table A-28 reveals that the dissociation equilibrium constants of CO_2, O_2, and N_2 are quite small and therefore may be neglected. (We learned from another source that the equilibrium constant for CO is also small). The combustion is then complete and the reaction is described by

Carbon + Air
25°C

$$\mathrm{C} + (\mathrm{O}_2 + 3.76\mathrm{N}_2) \longrightarrow \mathrm{CO}_2 + 3.76\mathrm{N}_2$$

The heat transfer for this combustion process is determined from the energy balance $E_{\mathrm{in}} - E_{\mathrm{out}} = \Delta E_{\mathrm{system}}$ applied on the combustion chamber with $W = 0$. It reduces to

$$-Q_{\mathrm{out}} = \sum N_P \left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_P - \sum N_R \left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_R$$

Assuming the air and the combustion products to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\bar{h}_f^\circ$ kJ/kmol	$\bar{h}_{298\mathrm{K}}$ kJ/kmol	$\bar{h}_{1000\mathrm{K}}$ kJ/kmol
N_2	0	8669	30,129
CO_2	-393,520	9364	42,769

Substituting,

$$\begin{aligned} -Q_{\mathrm{out}} &= (1)(-393{,}520 + 42{,}769 - 9364) + (3.76)(0 + 30{,}129 - 8669) \\ &= -279{,}400 \text{ kJ/kmol C} \end{aligned}$$

or
$$Q_{\mathrm{out}} = \frac{279{,}400 \text{ kJ/kmol}}{12 \text{ kg/kmol}} = \mathbf{23{,}280\ kJ/kg\ C}$$

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16-99 Methane gas is burned with 30 percent excess air. The equilibrium composition of the products of combustion and the amount of heat released by this combustion are to be determined.

Assumptions **1** The equilibrium composition consists of CO_2, H_2O, O_2, NO, and N_2. **2** The constituents of the mixture are ideal gases.

Analysis Inspection of the equilibrium constants of the possible reactions indicate that only the formation of NO need to be considered in addition to other complete combustion products. Then, the stoichiometric and actual reactions in this case are

Stoichiometric: $\quad N_2 + O_2 \Leftrightarrow 2NO \quad (\text{thus } \nu_{N2} = 1,\ \nu_{O2} = 1,\ \text{and } \nu_{NO} = 2)$

Actual: $\quad CH_4 + 2.6(O_2 + 3.76N_2) \longrightarrow CO_2 + 2H_2O + xNO + yO_2 + zN_2$

N balance: $\quad 9.776 = x + 2z \longrightarrow z = 4.888 - 0.5x$

O balance: $\quad 5.2 = 2 + 2 + x + 2y \longrightarrow y = 0.6 - 0.5x$

Total number of moles: $\quad N_{\text{total}} = 1 + 2 + x + y + z = 8.488$

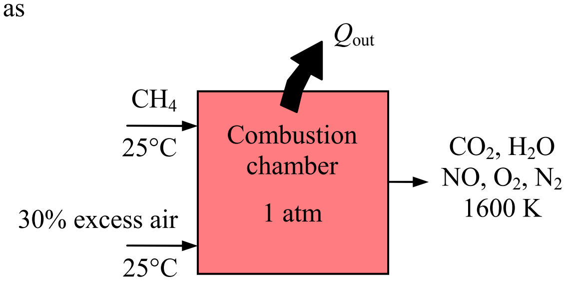
The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{NO}^{\nu_{NO}}}{N_{N2}^{\nu_{N2}} N_{O2}^{\nu_{O2}}} \left(\frac{P}{N_{\text{total}}} \right)^{(\nu_{NO} - \nu_{N2} - \nu_{O2})}$$

From Table A-28, at 1600 K, $\ln K_p = -5.294$.

Since the stoichiometric reaction being considered is double this reaction,

$$K_p = \exp(-2 \times 5.294) = 2.522 \times 10^{-5}$$



Substituting,

$$2.522 \times 10^{-5} = \frac{x^2}{(0.6 - 0.5x)(4.888 - 0.5x)} \left(\frac{1}{8.488} \right)^{2-1-1}$$

Solving for x,

$$x = 0.008566$$

Then,

$$y = 0.6 - 0.5x = 0.5957$$
$$z = 4.888 - 0.5x = 4.884$$

Therefore, the equilibrium composition of the products mixture at 1600 K and 1 atm is

$$\mathbf{CH_4 + 2.6(O_2 + 3.76N_2) \longrightarrow CO_2 + 2H_2O + 0.008566NO + 0.5957O_2 + 4.884N_2}$$

The heat transfer for this combustion process is determined from the energy balance $E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$ applied on the combustion chamber with $W = 0$. It reduces to

$$-Q_{\text{out}} = \sum N_P \left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ \right)_P - \sum N_R \left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ \right)_R$$

Assuming the air and the combustion products to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\bar{h}_f^\circ$ kJ/kmol	$\bar{h}_{298K}$ kJ/kmol	$\bar{h}_{1600K}$ kJ/kmol
CH_4	-74,850	---	---
O_2	0	8682	52,961
N_2	0	8669	50,571
H_2O	-241,820	9904	62,748
CO_2	-393,520	9364	76,944

Neglecting the effect of NO in the energy balance and substituting,

$$\begin{aligned} -Q_{\text{out}} &= (1)(-393{,}520 + 76{,}944 - 9364) + (2)(-241{,}820 + 62{,}748 - 9904) + 0.5957(52{,}961 - 8682) \\ &\quad + (4.884)(50{,}571 - 8669) - (-74{,}850) \\ &= -472{,}900 \text{ kJ/kmol } CH_4 \end{aligned}$$

or $\quad Q_{\text{out}} = \mathbf{472{,}900\ kJ/kmol\ CH_4}$

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16-100 Propane gas is burned with 30% excess air. The equilibrium composition of the products of combustion and the amount of heat released by this combustion are to be determined.

Assumptions **1** The equilibrium composition consists of CO_2, H_2O, O_2, NO, and N_2. **2** The constituents of the mixture are ideal gases.

Analysis (*a*) The stoichiometric and actual reactions in this case are

Stoichiometric: $N_2 + O_2 \Leftrightarrow 2NO$ (thus $\nu_{N2} = 1,\ \nu_{O2} = 1,\ \text{and}\ \nu_{NO} = 2$)

Actual: $C_3H_8 + 1.3\times 5(O_2 + 3.76N_2) \longrightarrow 3CO_2 + 4H_2O + x\text{NO} + yO_2 + zN_2$

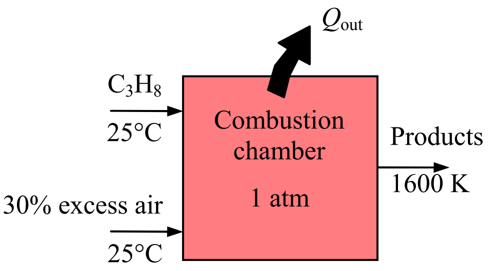
N balance: $48.88 = x + 2z \longrightarrow z = 24.44 - 0.5x$

O balance: $13 = 6 + 4 + x + 2y \longrightarrow y = 1.5 - 0.5x$

Total number of moles: $N_{\text{total}} = 3 + 4 + x + y + z = 32.94$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{NO}^{\nu_{NO}}}{N_{N2}^{\nu_{N2}} N_{O2}^{\nu_{O2}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{NO}-\nu_{N2}-\nu_{O2})}$$



From Table A-28, at 1600 K, $\ln K_p = -5.294$.

Since the stoichiometric reaction being considered is double this reaction,

$$K_p = \exp(-2\times 5.294) = 2.522\times 10^{-5}$$

Substituting,

$$2.522\times 10^{-5} = \frac{x^2}{(1.5-0.5x)(24.44-0.5x)}\left(\frac{1}{32.94}\right)^{2-1-1}$$

Solving for *x*,

$x = 0.03024$

Then,

$y = 1.5 - 0.5x = 1.485$

$z = 24.44 - 0.5x = 24.19$

Therefore, the equilibrium composition of the products mixture at 1600 K and 1 atm is

$$\mathbf{C_3H_8 + 6.5(O_2 + 3.76N_2) \longrightarrow 3CO_2 + 4H_2O + 0.03024NO + 1.485O_2 + 24.19N_2}$$

(*b*) The heat transfer for this combustion process is determined from the energy balance $E_{in} - E_{out} = \Delta E_{\text{system}}$ applied on the combustion chamber with $W = 0$. It reduces to

$$-Q_{out} = \sum N_P\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_P - \sum N_R\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ\right)_R$$

Assuming the air and the combustion products to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\bar{h}_f^\circ$ kJ/kmol	$\bar{h}_{298K}$ kJ/kmol	$\bar{h}_{1600K}$ kJ/kmol
C_3H_8	-103,850	---	---
O_2	0	8682	52,961
N_2	0	8669	50,571
H_2O	-241,820	9904	62,748
CO_2	-393,520	9364	76,944

Neglecting the effect of NO in the energy balance and substituting,

$$\begin{aligned}-Q_{out} &= (3)(-393{,}520 + 76{,}944 - 9364) + (4)(-241{,}820 + 62{,}748 - 9904) + 1.485(52{,}961 - 8682)\\ &\quad + (24.19)(50{,}571 - 8669) - (-103{,}850)\\ &= -654{,}360\ \text{kJ/kmol}\ C_3H_8\end{aligned}$$

or $$Q_{out} = \frac{654{,}360\ \text{kJ/kmol}}{44\ \text{kg/kmol}} = \mathbf{14{,}870\ kJ/kg\ C_3H_8}$$

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16-101E Gaseous octane gas is burned with 40% excess air. The equilibrium composition of the products of combustion is to be determined.

Assumptions **1** The equilibrium composition consists of CO_2, H_2O, O_2, NO, and N_2. **2** The constituents of the mixture are ideal gases.

Analysis The stoichiometric and actual reactions in this case are

Stoichiometric: $N_2 + O_2 \Leftrightarrow 2NO$ (thus $\nu_{N2} = 1,\ \nu_{O2} = 1,$ and $\nu_{NO} = 2$)

Actual: $C_8H_{18} + 1.4\times 12.5(O_2 + 3.76N_2) \longrightarrow 8CO_2 + 9H_2O + x\mathrm{NO} + yO_2 + zN_2$

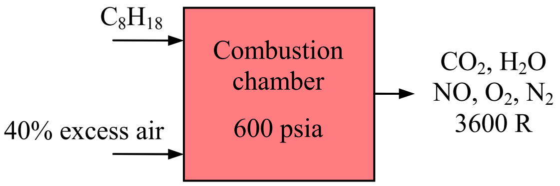
N balance: $131.6 = x + 2z \longrightarrow z = 65.8 - 0.5x$

O balance: $35 = 16 + 9 + x + 2y \longrightarrow y = 5 - 0.5x$

Total number of moles: $N_{\text{total}} = 8 + 9 + x + y + z = 87.8$

The equilibrium constant relation can be expressed as

$$K_p = \frac{N_{NO}^{\nu_{NO}}}{N_{N2}^{\nu_{N2}} N_{O2}^{\nu_{O2}}} \left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{NO} - \nu_{N2} - \nu_{O2})}$$



From Table A-28, at 2000 K (3600 R), $\ln K_p = -3.931$. Since the stoichiometric reaction being considered is double this reaction,

$$K_p = \exp(-2\times 3.931) = 3.851\times 10^{-4}$$

Substituting,

$$3.851\times 10^{-4} = \frac{x^2}{(5 - 0.5x)(65.8 - 0.5x)} \left(\frac{600/14.7}{87.8}\right)^{2-1-1}$$

Solving for x,

$$x = 0.1119$$

Then,

$$y = 5 - 0.5x = 4.944$$

$$z = 65.8 - 0.5x = 65.74$$

Therefore, the equilibrium composition of the products mixture at 3600 R and 600 psia is

$$\mathbf{C_8H_{18} + 17.5(O_2 + 3.76N_2) \longrightarrow 8CO_2 + 9H_2O + 0.1119NO + 4.944O_2 + 65.74N_2}$$

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16-102 A mixture of H_2O and O_2 is heated to a high temperature. The equilibrium composition is to be determined.

Assumptions **1** The equilibrium composition consists of H_2O, 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

$$2H_2O + 3O_2 \longrightarrow x\,H_2O + y\,H_2 + z\,O_2 + w\,OH$$

Mass balances for hydrogen and oxygen yield

H balance: $4 = 2x + 2y + w$ (1)

O balance: $8 = x + 2z + w$ (2)

H_2O, OH, H_2, O_2
3600 K
8 atm

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

$$H_2O \Leftrightarrow H_2 + \tfrac{1}{2}O_2 \qquad \text{(reaction 1)}$$

$$H_2O \Leftrightarrow \tfrac{1}{2}H_2 + OH \qquad \text{(reaction 2)}$$

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

$$\ln K_{P1} = -1.392 \longrightarrow K_{P1} = 0.24858$$

$$\ln K_{P2} = -1.088 \longrightarrow K_{P2} = 0.33689$$

The K_P relations for these two simultaneous reactions are

$$K_{P1} = \frac{N_{H_2}^{\nu_{H2}} N_{O_2}^{\nu_{O2}}}{N_{H_2O}^{\nu_{H2O}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{H2}+\nu_{O2}-\nu_{H2O})}$$

$$K_{P2} = \frac{N_{H_2}^{\nu_{H2}} N_{OH}^{\nu_{OH}}}{N_{H_2O}^{\nu_{H2O}}}\left(\frac{P}{N_{\text{total}}}\right)^{(\nu_{H2}+\nu_{OH}-\nu_{H2O})}$$

where

$$N_{\text{total}} = N_{H_2O} + N_{H_2} + N_{O_2} + N_{OH} = x + y + z + w$$

Substituting,

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

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

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

$x = 1.371$ $y = 0.1646$ $z = 2.85$ $w = 0.928$

Therefore, the equilibrium composition becomes

$$\mathbf{1.371H_2O + 0.165H_2 + 2.85O_2 + 0.928OH}$$

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16-103 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

$$3\mathrm{C_2O} + 3\mathrm{O_2} \longrightarrow x\,\mathrm{CO_2} + y\,\mathrm{CO} + z\,\mathrm{O_2} + w\,\mathrm{O}$$

CO_2, CO, O_2, O
3400 K
2 atm

Mass balances for carbon and oxygen yield

C balance: $3 = x + y$ (1)

O balance: $12 = 2x + y + 2z + w$ (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

$$\mathrm{CO_2} \Leftrightarrow \mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \qquad \text{(reaction 1)}$$

$$\mathrm{O_2} \Leftrightarrow 2\mathrm{O} \qquad \text{(reaction 2)}$$

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

$$\ln K_{P1} = 0.169 \longrightarrow K_{P1} = 1.1841$$

$$\ln K_{P2} = -1.935 \longrightarrow K_{P2} = 0.1444$$

The K_P relations for these two simultaneous reactions are

$$K_{P1} = \frac{N_{\mathrm{CO}}^{\nu_{\mathrm{CO}}} N_{\mathrm{O_2}}^{\nu_{\mathrm{O_2}}}}{N_{\mathrm{CO_2}}^{\nu_{\mathrm{CO_2}}}} \left(\frac{P}{N_{\text{total}}} \right)^{(\nu_{\mathrm{CO}} + \nu_{\mathrm{O_2}} - \nu_{\mathrm{CO_2}})}$$

$$K_{P2} = \frac{N_{\mathrm{O}}^{\nu_{\mathrm{O}}}}{N_{\mathrm{O_2}}^{\nu_{\mathrm{O_2}}}} \left(\frac{P}{N_{\text{total}}} \right)^{\nu_{\mathrm{O}} - \nu_{\mathrm{O_2}}}$$

where

$$N_{\text{total}} = N_{\mathrm{CO_2}} + N_{\mathrm{O_2}} + N_{\mathrm{CO}} + N_{\mathrm{O}} = x + y + z + w$$

Substituting,

$$1.1841 = \frac{(y)(z)^{1/2}}{x} \left(\frac{2}{x + y + z + w} \right)^{1/2} \qquad (3)$$

$$0.1444 = \frac{w^2}{z} \left(\frac{2}{x + y + z + w} \right)^{2-1} \qquad (4)$$

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

$x = 1.313$ $y = 1.687$ $z = 3.187$ $w = 1.314$

Thus the equilibrium composition is

$$\mathbf{1.313CO_2 + 1.687CO + 3.187O_2 + 1.314O}$$

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16-104 EES Problem 16-103 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 anwers 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*1 +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 pressrues."

Call JANAF('O',T_prod:Cp,h_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"
```

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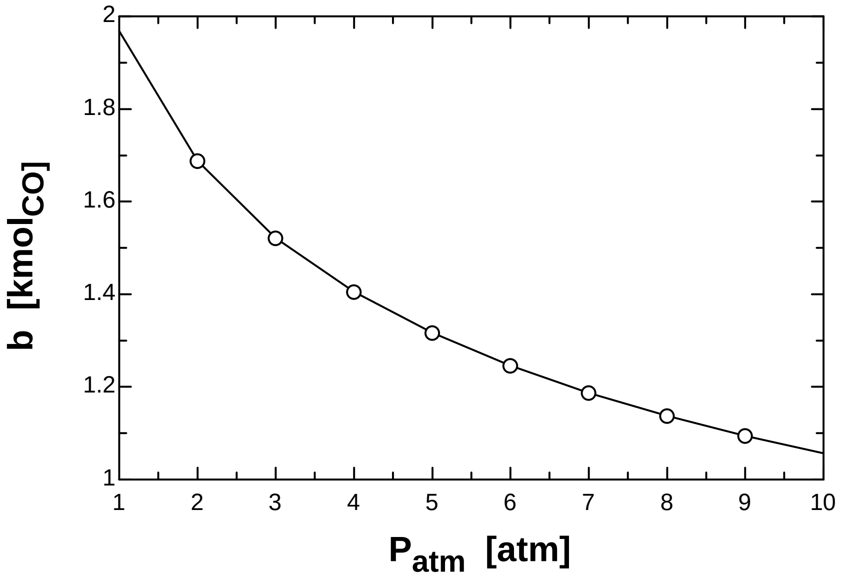
```
"The equilibrium constant is also given by Eq. 15-15."
"Write the equilibrium constant for the following system of equations:
3 CO2 + 3 O2=aCO2 +bCO + cO2+dO
CO2=CO+0.5O2
O2=2O"

"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
```

b [kmol_{CO}]	P_{atm} [atm]
1.968	1
1.687	2
1.52	3
1.404	4
1.315	5
1.244	6
1.186	7
1.136	8
1.093	9
1.055	10



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16-105 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 H_2 can be expressed as

$$H_2 + \tfrac{1}{2}O_2 \Leftrightarrow H_2O$$

The $\overline{h}_R$ of the combustion process of H_2 at 2400 K is the amount of energy released as one kmol of H_2 is burned in a steady-flow combustion chamber at a temperature of 2400 K, and can be determined from

$$\overline{h}_R = \sum N_P\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)_P - \sum N_R\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)_R$$

Assuming the H_2O, H_2, and O_2 to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\overline{\mathbf{h}}_\mathbf{f}^\circ$ **kJ/kmol**	$\overline{\mathbf{h}}_{\mathbf{298\ K}}$ **kJ/kmol**	$\overline{\mathbf{h}}_{\mathbf{2400\ K}}$ **kJ/kmol**
H_2O	-241,820	9904	103,508
H_2	0	8468	75,383
O_2	0	8682	83,174

Substituting,

$$\begin{aligned}\overline{h}_R &= 1(-241{,}820 + 103{,}508 - 9904)\\ &\quad - 1(0 + 75{,}383 - 8468)\\ &\quad - 0.5(0 + 83{,}174 - 8682)\\ &= \mathbf{-252{,}377\ kJ/kmol}\end{aligned}$$

(*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,

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

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

$$\overline{h}_R \cong \mathbf{-252{,}047\ \ kJ/kmol}$$

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16-106 EES Problem 16-105 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_prod=2400 [K]
DELTAT_prod =25 [K]
R_u=8.314 [kJ/kmol-K]
T_prod_1 = T_prod - DELTAT_prod
T_prod_2 = T_prod + DELTAT_prod

"The combustion equation is
1 H2 + 0.5 O2 =>1 H2O"
"The enthalpy of reaction H_bar_R using enthalpy data is:"
h_bar_R_Enthalpy = HP - HR
HP = 1*Enthalpy(H2O,T=T_prod )
HR = 1*Enthalpy(H2,T=T_prod ) + 0.5*Enthalpy(O2,T=T_prod )

"The enthalpy of reaction H_bar_R using enthalpy data is found using the following equilibruim
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_H2O_1=Enthalpy(H2O,T=T_prod_1 )-T_prod_1 *Entropy(H2O,T=T_prod_1 ,P=101.3)
g_H2_1=Enthalpy(H2,T=T_prod_1 )-T_prod_1 *Entropy(H2,T=T_prod_1 ,P=101.3)
g_O2_1=Enthalpy(O2,T=T_prod_1 )-T_prod_1 *Entropy(O2,T=T_prod_1 ,P=101.3)
g_H2O_2=Enthalpy(H2O,T=T_prod_2 )-T_prod_2 *Entropy(H2O,T=T_prod_2 ,P=101.3)
g_H2_2=Enthalpy(H2,T=T_prod_2 )-T_prod_2 *Entropy(H2,T=T_prod_2 ,P=101.3)
g_O2_2=Enthalpy(O2,T=T_prod_2 )-T_prod_2 *Entropy(O2,T=T_prod_2 ,P=101.3)

"The standard-state (at 1 atm) Gibbs functions are"
DELTAG_1 =1*g_H2O_1-0.5*g_O2_1-1*g_H2_1
DELTAG_2 =1*g_H2O_2-0.5*g_O2_2-1*g_H2_2

"The equilibrium constants are given by Eq. 15-14."
K_p_1 = exp(-DELTAG_1/(R_u*T_prod_1)) "From EES data"
K_P_2 = exp(-DELTAG_2/(R_u*T_prod_2)) "From EES data"

"the entahlpy of reaction is estimated from the equilibrium constant K_p by using EQ 15-18 as:"
ln(K_P_2/K_P_1)=h_bar_R_Kp/R_u*(1/T_prod_1 - 1/T_prod_2)
PercentError = ABS((h_bar_R_enthalpy - h_bar_R_Kp)/h_bar_R_enthalpy)*Convert(, %)
```

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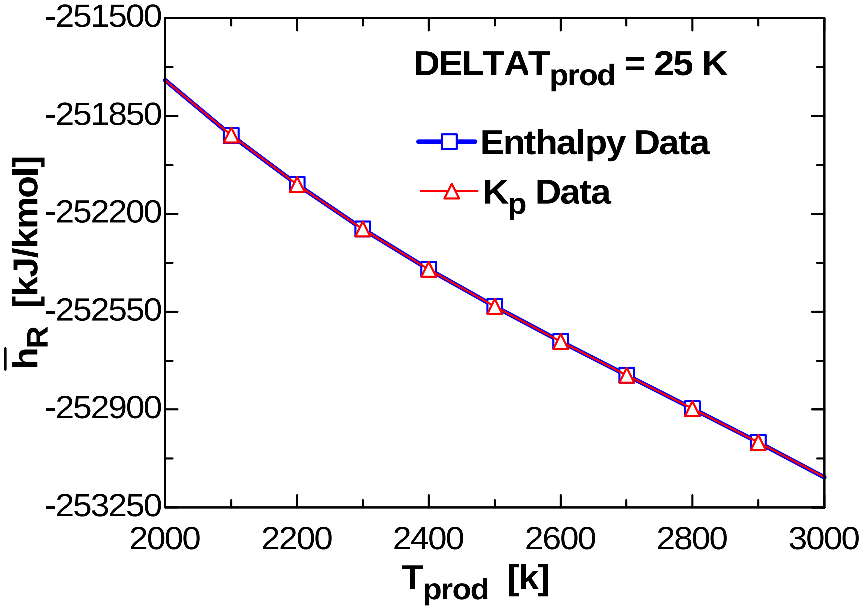
Percent Error [%]	T_{prod} [K]	$h_{REnthalpy}$ [kJ/kmol]	h_{RKp} [kJ/kmol]
0.0002739	2000	-251723	-251722
0.0002333	2100	-251920	-251919
0.000198	2200	-252096	-252095
0.0001673	2300	-252254	-252254
0.0001405	2400	-252398	-252398
0.0001173	2500	-252532	-252531
0.00009706	2600	-252657	-252657
0.00007957	2700	-252778	-252777
0.00006448	2800	-252897	-252896
0.00005154	2900	-253017	-253017
0.0000405	3000	-253142	-253142



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16-107 The K_P value of the dissociation process $O_2 \Leftrightarrow 2O$ 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

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

The $\overline{h}_R$ of the specified reaction at 2800 K is the amount of energy released as one kmol of O_2 dissociates in a steady-flow combustion chamber at a temperature of 2800 K, and can be determined from

$$\overline{h}_R = \sum N_P\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)_P - \sum N_R\left(\overline{h}_f^\circ + \overline{h} - \overline{h}^\circ\right)_R$$

Assuming the O_2 and O to be ideal gases, we have $h = h(T)$. From the tables,

Substance	$\overline{\mathbf{h}}_\mathbf{f}^\circ$ **kJ/kmol**	$\overline{\mathbf{h}}_{\mathbf{298\ K}}$ **kJ/kmol**	$\overline{\mathbf{h}}_{\mathbf{2800\ K}}$ **kJ/kmol**
O	249,190	6852	59,241
O_2	0	8682	98,826

Substituting,

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

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

$$K_{P2} = \mathbf{0.0128}$$

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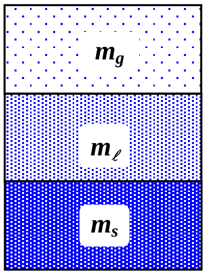
16-108 It is to be shown that when the three phases of a pure substance are in equilibrium, the specific Gibbs function of each phase is the same.

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

$$G = m_s g_s + m_\ell g_\ell + m_g g_g$$

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

$$dG = g_s dm_s + g_\ell dm_\ell + g_g dm_g$$



From conservation of mass,

$$dm_s + dm_\ell + dm_g = 0 \quad \longrightarrow \quad dm_s = -dm_\ell - dm_g$$

Substituting,

$$dG = -g_s(dm_\ell + dm_g) + g_\ell dm_\ell + g_g dm_g$$

Rearranging,

$$dG = (g_\ell - g_s)dm_\ell + (g_g - g_s)dm_g$$

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

$$g_\ell = g_s \quad \text{and} \quad g_g = g_s$$

Combining these two conditions gives the desired result,

$$g_\ell = g_s = g_s$$

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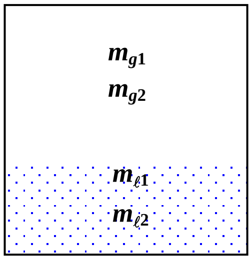
16-109 It is to be shown that when the two phases of a two-component system are in equilibrium, the specific Gibbs function of each phase of each component is the same.

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

$$G = (m_{\ell 1} g_{\ell 1} + m_{g1} g_{g1}) + (m_{\ell 2} g_{\ell 2} + m_{g2} g_{g2})$$



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

$$dG = g_{\ell 1} dm_{\ell 1} + g_{g1} dm_{g1} + g_{\ell 2} dm_{\ell 2} + g_{g2} dm_{g2}$$

From conservation of mass,

$$dm_{g1} = -dm_{\ell 1} \quad \text{and} \quad dm_{g2} = -dm_{\ell 2}$$

Substituting,

$$dG = (g_{\ell 1} - g_{g1}) dm_{\ell 1} + (g_{\ell 2} - g_{g2}) dm_{\ell 2}$$

For equilibrium, $dG = 0$. Also $dm_{\ell 1}$ and $dm_{\ell 2}$ can be varied independently. Thus each term on the right hand side must be zero to satisfy the equilibrium criteria. Then we have

$$g_{\ell 1} = g_{g1} \quad \text{and} \quad g_{\ell 2} = g_{g2}$$

which is the desired result.

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16-110 A mixture of CO and O_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_2 and O_2. **2** Both the reactants and the products are ideal gases.

CO_2, CO, O_2
25°C
2 atm

Analysis The combustion equation can be written as

$$\mathrm{CO} + 3\mathrm{O}_2 \longrightarrow \mathrm{CO}_2 + 2.5\mathrm{O}_2$$

The heat transfer can be determined from

$$-Q_{\text{out}} = \sum N_P\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{\boldsymbol{v}}\right)_P - \sum N_R\left(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ - P\bar{\boldsymbol{v}}\right)_R$$

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 $P\bar{\boldsymbol{v}}$ terms in this equation can be replaced by R_uT. It yields

$$-Q_{\text{out}} = \sum N_P\left(\bar{h}_f^\circ + \bar{h}_{500\text{ K}} - \bar{h}_{298\text{ K}} - R_uT\right)_P - \sum N_R\left(\bar{h}_f^\circ - R_uT\right)_R$$

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

Substance	$\mathbf{\bar{h}_f^\circ}$ **kJ/kmol**	$\mathbf{\bar{h}_{298\text{ K}}}$ **kJ/kmol**	$\mathbf{\bar{h}_{500\text{ K}}}$ **kJ/kmol**
CO	-110,530	8669	14,600
O_2	0	8682	14,770
CO_2	-393,520	9364	17,678

Substituting,

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

or

$$Q_{\text{out}} = \mathbf{264{,}095\ kJ/kmol\ CO}$$

The final pressure in the tank is determined from

$$\frac{P_1\mathbf{V}}{P_2\mathbf{V}} = \frac{N_1R_uT_1}{N_2R_uT_2} \longrightarrow P_2 = \frac{N_2T_2}{N_1T_1}P_1 = \frac{3.5}{4}\times\frac{500\text{ K}}{298\text{ K}}(2\text{ atm}) = \mathbf{2.94\ atm}$$

The equilibrium constant for the reaction $\mathrm{CO} + \frac{1}{2}\mathrm{O}_2 \Leftrightarrow \mathrm{CO}_2$ 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.

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16-111 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

$$y_{\text{i, liquid side}}(0) = \frac{P_{\text{i, gas side}}(0)}{H}$$

Henry's constant H increases with temperature, and thus the fraction of gas i in the liquid $y_{\text{i,liquid side}}$ decreases. Therefore, heating a liquid will drive off the dissolved gases in a liquid.

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16-112 A 2-L bottle is filled with carbonated drink that is fully charged (saturated) with CO_2 gas. The volume that the CO_2 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 CO_2 gas and the water vapor are ideal gases. **3** The CO_2 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 CO_2 dissolved in water at 17ºC (290 K) is H = 1280 bar (Table 16-2). Molar masses of CO_2 and water are 44.01 and 18.015 kg/kmol, respectively (Table A-1). The gas constant of CO_2 is 0.1889 kPa.m^3/kg.K. Also, 1 bar = 100 kPa.

Analysis In the charging station, the CO_2 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 CO_2 gas is

$$P_{\text{CO}_2\text{, gas side}} = P - P_{\text{vapor}} = P - P_{\text{sat @ 17°C}} = 600 - 1.938 = 598.06 \text{ kPa} = 5.9806 \text{ bar}$$

From Henry's law, the mole fraction of CO_2 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

$$w_i = \frac{m_i}{m_m} = \frac{N_i M_i}{N_m M_m} = y_i \frac{M_i}{M_m}$$

where the apparent molar mass of the drink (liquid water - CO_2 mixture) is

$$\begin{aligned} M_m &= \sum y_i M_i = y_{\text{liquid water}} M_{\text{water}} + y_{\text{CO}_2} M_{\text{CO}_2} \\ &= 0.99533 \times 18.015 + 0.00467 \times 44.01 = 18.14 \text{ kg/kmol} \end{aligned}$$

Then the mass fraction of dissolved CO_2 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 CO_2 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 CO_2 at the room conditions of 20°C and 100 kPa becomes

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

Discussion Note that the amount of dissolved CO_2 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 CO_2 in the drink.

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16-113 EES Ethyl alcohol C_2H_5OH (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

$$\mathrm{C_2H_5OH\,(gas)} + (1+Ex)a_{\text{th}}\left[\mathrm{O_2} + 3.76\mathrm{N_2}\right] \longrightarrow 2\,\mathrm{CO_2} + 3\,\mathrm{H_2O} + (Ex)(a_{\text{th}})\,\mathrm{O_2} + f\,\mathrm{N_2}$$

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

$$1 + (1+Ex)a_{\text{th}} \times 2 = 2\times 2 + 3\times 1 + (Ex)(a_{\text{th}})\times 2$$

The reaction equation with products in equilibrium is

$$\mathrm{C_2H_5OH\,(gas)} + (1+Ex)a_{\text{th}}\left[\mathrm{O_2} + 3.76\mathrm{N_2}\right] \longrightarrow a\,\mathrm{CO_2} + b\,\mathrm{CO} + d\,\mathrm{H_2O} + e\,\mathrm{O_2} + f\,\mathrm{N_2}$$

The coefficients are determined from the mass balances

Carbon balance: $2 = a + b$

Hydrogen balance: $6 = 2d \longrightarrow d = 3$

Oxygen balance: $1 + (1+Ex)a_{\text{th}} \times 2 = a\times 2 + b + d + e\times 2$

Nitrogen balance: $(1+Ex)a_{\text{th}} \times 3.76 = f$

Solving the above equations, we find the coefficients to be

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

Then, we write the balanced reaction equation as

$$\mathrm{C_2H_5OH\,(gas)} + 4.2\left[\mathrm{O_2} + 3.76\mathrm{N_2}\right] \longrightarrow 1.995\,\mathrm{CO_2} + 0.004938\,\mathrm{CO} + 3\,\mathrm{H_2O} + 1.202\,\mathrm{O_2} + 15.79\,\mathrm{N_2}$$

Total moles of products at equilibrium are

$$N_{\text{tot}} = 1.995 + 0.004938 + 3 + 1.202 + 15.79 = 21.99$$

The assumed equilibrium reaction is

$$\mathrm{CO_2} \longleftrightarrow \mathrm{CO} + 0.5\mathrm{O_2}$$

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

$$\Delta G^*(T) = \nu_{\text{CO}}\,\bar{g}^*_{\text{CO}}(T_{\text{prod}}) + \nu_{\text{O2}}\,\bar{g}^*_{\text{O2}}(T_{\text{prod}}) - \nu_{\text{CO2}}\,\bar{g}^*_{\text{CO2}}(T_{\text{prod}})$$

and the Gibbs functions are defined as

$$\bar{g}^*_{\text{CO}}(T_{\text{prod}}) = (\bar{h} - T_{\text{prod}}\bar{s})_{\text{CO}}$$
$$\bar{g}^*_{\text{O2}}(T_{\text{prod}}) = (\bar{h} - T_{\text{prod}}\bar{s})_{\text{O2}}$$
$$\bar{g}^*_{\text{CO2}}(T_{\text{prod}}) = (\bar{h} - T_{\text{prod}}\bar{s})_{\text{CO2}}$$

The equilibrium constant is also given by

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

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A steady flow energy balance gives

$$H_R = H_P$$

where

$$\begin{aligned} H_R &= \bar{h}^o_{f\ \text{fuel@25°C}} + 4.2\bar{h}_{\text{O2@25°C}} + 15.79\bar{h}_{\text{N2@25°C}} \\ &= (-235{,}310 \text{ kJ/kmol}) + 4.2(0) + 15.79(0) = -235{,}310 \text{ kJ/kmol} \end{aligned}$$

$$H_P = 1.995\bar{h}_{\text{CO2@}T_{\text{prod}}} + 0.004938\bar{h}_{\text{CO@}T_{\text{prod}}} + 3h_{\text{H2O@}T_{\text{prod}}} + 1.202\bar{h}_{\text{O2@}T_{\text{prod}}} + 15.79\bar{h}_{\text{N2@}T_{\text{prod}}}$$

Solving the energy balance equation using EES, we obtain the adiabatic flame temperature to be

$$T_{\text{prod}} = \mathbf{1907\ K}$$

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

```
"The product temperature isT_prod"
"The reactant temperature is:"
T_reac= 25+273.15 "[K]"
"For adiabatic combustion of 1 kmol of fuel: "
Q_out = 0 "[kJ]"
PercentEx = 40  "Percent excess air"
Ex = PercentEx/100  "EX = % Excess air/100"
P_prod =101.3"[kPa]"
R_u=8.314 "[kJ/kmol-K]"
"The complete combustion reaction equation for excess air  is:"
"C2H5OH(gas)+ (1+Ex)*A_th (O2 +3.76N2)=2 CO2 +  3 H2O +Ex*A_th O2 + f N2"
"Oxygen Balance for complete combustion:"
1 + (1+Ex)*A_th*2=2*2+3*1 + Ex*A_th*2
"The reaction equation for excess air and products in equilibrium is:"
"C2H5OH(gas)+ (1+Ex)*A_th (O2 +3.76N2)=a CO2 + b CO+ d H2O + e O2 + f N2"
"Carbon Balance:"
2=a + b
"Hydrogen Balance:"
6=2*d
"Oxygen Balance:"
1 + (1+Ex)*A_th*2=a*2+b + d + e*2
"Nitrogen Balance:"
(1+Ex)*A_th*3.76 = f
N_tot =a +b + d + e + f  "Total kilomoles of products at equilibrium"
"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=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)
"The standard-state Gibbs function is"
DELTAG =1*g_CO+0.5*g_O2-1*g_CO2
"The equilibrium constant is given by Eq. 15-14."
K_P  = exp(-DELTAG /(R_u*T_prod ))
P=P_prod /101.3"atm"
"The equilibrium constant is also given by Eq. 15-15."
```

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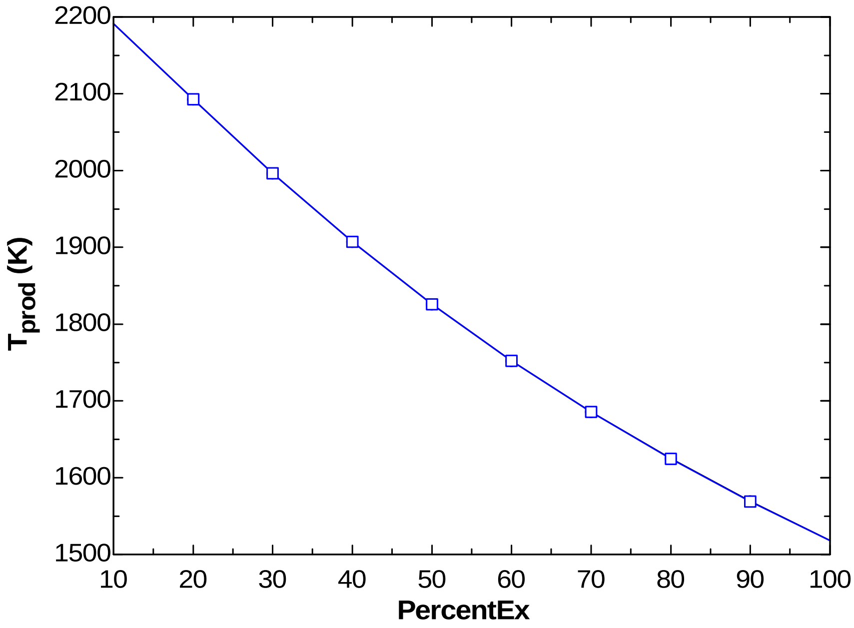
```
"K_ P = (P/N_tot)^(1+0.5-1)*(b^1*e^0.5)/(a^1)"
sqrt(P/N_tot )*b *sqrt(e )=K_P *a
"The steady-flow energy balance is:"
H_R = Q_out+H_P
h_bar_f_C2H5OHgas=-235310 "[kJ/kmol]"
H_R=1*(h_bar_f_C2H5OHgas )
+(1+Ex)*A_th*ENTHALPY(O2,T=T_reac)+(1+Ex)*A_th*3.76*ENTHALPY(N2,T=T_reac)
"[kJ/kmol]"
H_P=a*ENTHALPY(CO2,T=T_prod)+b*ENTHALPY(CO,T=T_prod)+d*ENTHALPY(H2O,T=T_prod)
+e*ENTHALPY(O2,T=T_prod)+f*ENTHALPY(N2,T=T_prod) "[kJ/kmol]"
```

a	a_{th}	b	d	e	f	PercentEx [%]	T_{prod} [K]
1.922	3	0.07809	3	0.339	12.41	10	2191
1.97	3	0.03017	3	0.6151	13.54	20	2093
1.988	3	0.01201	3	0.906	14.66	30	1996
1.995	3	0.004933	3	1.202	15.79	40	1907
1.998	3	0.002089	3	1.501	16.92	50	1826
1.999	3	0.0009089	3	1.8	18.05	60	1752
2	3	0.000405	3	2.1	19.18	70	1685
2	3	0.0001843	3	2.4	20.3	80	1625
2	3	0.0000855	3	2.7	21.43	90	1569
2	3	0.00004036	3	3	22.56	100	1518



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16-114 EES 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

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

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

$$C_8H_{18} + P_{th}a_{th}[O_2 + 3.76N_2] \longrightarrow a\,CO_2 + b\,CO + d\,H_2O + e\,O_2 + f\,N_2$$

The coefficients are to be determined from the mass balances

Carbon balance: $8 = a + b$

Hydrogen balance: $18 = 2d \longrightarrow d = 9$

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

$$CO_2 \longleftrightarrow CO + 0.5O_2$$

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

$$\bar{g}^*_{CO}(T_{prod}) = (\bar{h} - T_{prod}\bar{s})_{CO} = (-53{,}826) - (2000)(258.48) = -570{,}781\text{ kJ/kmol}$$
$$\bar{g}^*_{O2}(T_{prod}) = (\bar{h} - T_{prod}\bar{s})_{O2} = (59{,}193) - (2000)(268.53) = -477{,}876\text{ kJ/kmol}$$
$$\bar{g}^*_{CO2}(T_{prod}) = (\bar{h} - T_{prod}\bar{s})_{CO2} = (-302{,}128) - (2000)(309.00) = -920{,}121\text{ kJ/kmol}$$

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

$$\begin{aligned}\Delta G^*(T_{prod}) &= \nu_{CO}\bar{g}^*_{CO}(T_{prod}) + \nu_{O2}\bar{g}^*_{O2}(T_{prod}) - \nu_{CO2}\bar{g}^*_{CO2}(T_{prod}) \\ &= 1(-570{,}781) + 0.5(-477{,}876) - (-920{,}121) = 110{,}402\text{ kJ/kmol}\end{aligned}$$

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

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

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$$H_R = 1\bar{h}_{\text{C8H18 @ 298 K}} + P_{\text{th}} a_{\text{th}} \bar{h}_{\text{O2 @ 298 K}} + (P_{\text{th}} a_{\text{th}} \times 3.76)\bar{h}_{\text{N2 @ 298 K}}$$
$$= (-208{,}459) + P_{\text{th}} a_{\text{th}}(0) + (P_{\text{th}} a_{\text{th}} \times 3.76)(0) = -208{,}459 \text{ kJ/kmol}$$
$$H_P = a\bar{h}_{\text{CO2 @ 2000 K}} + b\bar{h}_{\text{CO @ 2000 K}} + d\bar{h}_{\text{H2O @ 2000 K}} + e\bar{h}_{\text{O2 @ 2000 K}} + f\,\bar{h}_{\text{N2 @ 2000 K}}$$
$$= a(-302{,}128) + b(-53{,}826) + d(-169{,}171) + e(59{,}193) + f(56{,}115)$$

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

$$P_{\text{th}} = 1.024,\ a_{\text{th}} = 12.5,\ a = 7.935,\ b = 0.06544,\ d = 9,\ e = 0.3289,\ f = 48.11$$
$$\text{PercentTh} = P_{\text{th}} \times 100 = 1.024 \times 100 = \mathbf{102.4\%}$$
$$Q_{\text{out}} = \mathbf{995{,}500\ kJ/kmol\ C_8H_{18}}$$

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

```
"The product temperature is:"
T_prod = 2000 "[K]"
"The reactant temperature is:"
T_reac= 25+273 "[K]"
"PercentTH is  Percent theoretical air"
Pth= PercentTh/100  "Pth = % theoretical air/100"
P_prod = 5 "[atm]" *convert(atm,kPa)"[kPa]"
R_u=8.314 "[kJ/kmol-K]"
"The complete combustion reaction equation for excess air  is:"
"C8H18+ Pth*A_th (O2 +3.76N2)=8 CO2 +  9 H2O +(Pth-1)*A_th O2 + f N2"
"Oxygen Balance for complete combustion:"
 Pth*A_th*2=8*2+9*1 + (Pth-1)*A_th*2
"The reaction equation for excess air and products in equilibrium is:"
"C8H18+ Pth*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:"
Pth*A_th*2=a*2+b + d + e*2
"Nitrogen Balance:"
Pth*A_th*3.76 = f
N_tot =a +b + d + e + f  "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=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)
"The standard-state Gibbs function is"
DELTAG =1*g_CO+0.5*g_O2-1*g_CO2
"The equilibrium constant is given by Eq. 15-14."
K_P  = exp(-DELTAG /(R_u*T_prod ))
```

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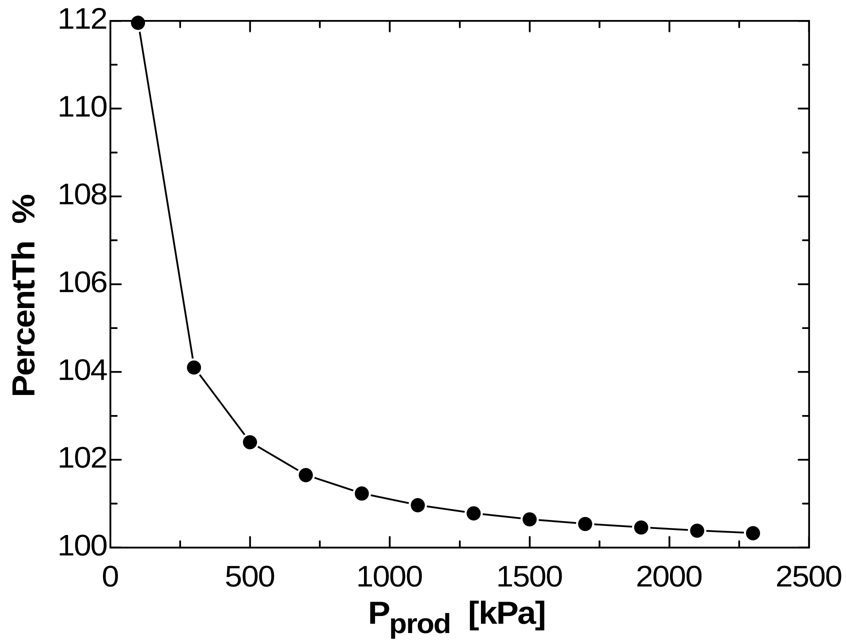
```
P=P_prod /101.3"atm"
"The equilibrium constant is also given by Eq. 15-15."
"K_ P = (P/N_tot)^(1+0.5-1)*(b^1*e^0.5)/(a^1)"
sqrt(P/N_tot )*b *sqrt(e )=K_P *a
"The steady-flow energy balance is:"
H_R = Q_out+H_P
H_R=1*ENTHALPY(C8H18,T=T_reac)+Pth*A_th*ENTHALPY(O2,T=T_reac)+Pth*A_th*3.76*ENTHALPY(N2,T=T_reac) "[kJ/kmol]"
H_P=a*ENTHALPY(CO2,T=T_prod)+b*ENTHALPY(CO,T=T_prod)+d*ENTHALPY(H2O,T=T_prod) +e*ENTHALPY(O2,T=T_prod)+f*ENTHALPY(N2,T=T_prod) "[kJ/kmol]"
```

P_{prod} [kPa]	PercentTh [%]
100	112
300	104.1
500	102.4
700	101.7
900	101.2
1100	101
1300	100.8
1500	100.6
1700	100.5
1900	100.5
2100	100.4
2300	100.3



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Fundamentals of Engineering (FE) Exam Problems

16-115 If the equilibrium constant for the reaction $H_2 + ½O_2 \rightarrow H_2O$ is K, the equilibrium constant for the reaction $2H_2O \rightarrow 2H_2 + O_2$ at the same temperature is

(a) $1/K$	(b) $1/(2K)$	(c) $2K$	(d) K^2	(e) $1/K^2$

Answer (e) $1/K^2$

16-116 If the equilibrium constant for the reaction $CO + ½O_2 \rightarrow CO_2$ is K, the equilibrium constant for the reaction $CO_2 + 3N_2 \rightarrow CO + ½O_2 + 3N_2$ at the same temperature is

(a) $1/K$	(b) $1/(K+3)$	(c) $4K$	(d) K	(e) $1/K^2$

Answer (a) $1/K$

16-117 The equilibrium constant for the reaction $H_2 + ½O_2 \rightarrow H_2O$ 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) $H_2 + ½O_2 \rightarrow H_2O$ at 5 atm,
(b) $2H_2 + O_2 \rightarrow 2H_2O$ at 1 atm,
(c) $H_2 + O_2 \rightarrow H_2O + ½O_2$ at 2 atm,
(d) $H_2 + ½O_2 + 3N_2 \rightarrow H_2O + 3N_2$ at 5 atm,
(e) $H_2 + ½O_2 + 3N_2 \rightarrow H_2O + 3N_2$ at 1 atm,

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

16-118 Of the reactions given below, the reaction whose equilibrium composition at a specified temperature is not affected by pressure is

(a) $H_2 + ½O_2 \rightarrow H_2O$
(b) $CO + ½O_2 \rightarrow CO_2$
(c) $N_2 + O_2 \rightarrow 2NO$
(d) $N_2 \rightarrow 2N$
(e) all of the above.

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

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16-119 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) $H_2 + ½O_2 \rightarrow H_2O$
(b) $CO + ½O_2 \rightarrow CO_2$
(c) $N_2 + O_2 \rightarrow 2NO$
(d) $N_2 \rightarrow 2N$
(e) none of the above.

Answer (d) $N_2 \rightarrow 2N$

16-120 Moist air is heated to a very high temperature. If the equilibrium composition consists of H_2O, O_2, N_2, OH, H_2, and 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

Answer (c) 3

16-121 Propane C_3H_8 is burned with air, and the combustion products consist of CO_2, CO, H_2O, O_2, N_2, OH, H_2, and 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

Answer (d) 4

16-122 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

Answer (d) 4

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16-123 The value of Henry's constant for 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 CO_2 by volume. Under phase equilibrium conditions, the mole fraction of CO_2 gas dissolved in water at 290 K is

(a) 2.3×10^{-4} (b) 3.0×10^{-4} (c) 0.80×10^{-4} (d) 2.2×10^{-4} (e) 5.6×10^{-4}

Answer (a) 2.3×10^{-4}

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).

```
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"
```

16-124 The solubility of nitrogen gas in rubber at 25°C is 0.00156 kmol/m^3·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/m^3 (b) 0.35 kg/m^3 (c) 0.42 kg/m^3 (d) 0.56 kg/m^3 (e) 0.078 kg/m^3

Answer (b) 0.35 kg/m^3

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).

```
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"
```

16-125 … 16-128 Design and Essay Problems

* * *

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