

# Chapter 16

## CHEMICAL AND PHASE EQUILIBRIUM

In Chapter 15 we analyzed combustion processes under the assumption that combustion is complete when there is sufficient time and oxygen. Often this is not the case, however. A chemical reaction may reach a state of equilibrium before reaching completion even when there is sufficient time and oxygen.

A system is said to be in *equilibrium* if no changes occur within the system when it is isolated from its surroundings. An isolated system is in *mechanical equilibrium* if no changes occur in pressure, in *thermal equilibrium* if no changes occur in temperature, in *phase equilibrium* if no transformations occur from one phase to another, and in *chemical equilibrium* if no changes occur in the chemical composition of the system. The conditions of mechanical and thermal equilibrium are straightforward, but the conditions of chemical and phase equilibrium can be rather involved.

The equilibrium criterion for reacting systems is based on the second law of thermodynamics; more specifically, the increase of entropy principle. For adiabatic systems, chemical equilibrium is established when the entropy of the reacting system reaches a maximum. Most reacting systems encountered in practice are not adiabatic, however. Therefore, we need to develop an equilibrium criterion applicable to any reacting system.

In this chapter, we develop a general criterion for chemical equilibrium and apply it to reacting ideal-gas mixtures. We then extend the analysis to simultaneous reactions. Finally, we discuss phase equilibrium for nonreacting systems.

### Objectives

The objectives of Chapter 16 are to:

- Develop the equilibrium criterion for reacting systems based on the second law of thermodynamics.
- Develop a general criterion for chemical equilibrium applicable to any reacting system based on minimizing the Gibbs function for the system.
- Define and evaluate the chemical equilibrium constant.
- Apply the general criterion for chemical equilibrium analysis to reacting ideal-gas mixtures.
- Apply the general criterion for chemical equilibrium analysis to simultaneous reactions.
- Relate the chemical equilibrium constant to the enthalpy of reaction.
- Establish the phase equilibrium for nonreacting systems in terms of the specific Gibbs function of the phases of a pure substance.
- Apply the Gibbs phase rule to determine the number of independent variables associated with a multicomponent, multiphase system.
- Apply Henry's law and Raoult's law for gases dissolved in liquids.

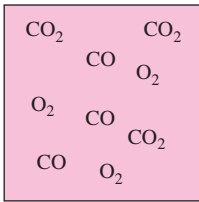
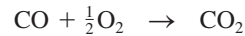


FIGURE 16-1

A reaction chamber that contains a mixture of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$  at a specified temperature and pressure.

## 16-1 ■ CRITERION FOR CHEMICAL EQUILIBRIUM

Consider a reaction chamber that contains a mixture of  $\text{CO}$ ,  $\text{O}_2$ , and  $\text{CO}_2$  at a specified temperature and pressure. Let us try to predict what will happen in this chamber (Fig. 16-1). Probably the first thing that comes to mind is a chemical reaction between  $\text{CO}$  and  $\text{O}_2$  to form more  $\text{CO}_2$ :



This reaction is certainly a possibility, but it is not the only possibility. It is also possible that some  $\text{CO}_2$  in the combustion chamber dissociated into  $\text{CO}$  and  $\text{O}_2$ . Yet a third possibility would be to have no reactions among the three components at all, that is, for the system to be in chemical equilibrium. It appears that although we know the temperature, pressure, and composition (thus the state) of the system, we are unable to predict whether the system is in chemical equilibrium. In this chapter we develop the necessary tools to correct this.

Assume that the  $\text{CO}$ ,  $\text{O}_2$ , and  $\text{CO}_2$  mixture mentioned above is in chemical equilibrium at the specified temperature and pressure. The chemical composition of this mixture does not change unless the temperature or the pressure of the mixture is changed. That is, a reacting mixture, in general, has different equilibrium compositions at different pressures and temperatures. Therefore, when developing a general criterion for chemical equilibrium, we consider a reacting system at a fixed temperature and pressure.

Taking the positive direction of heat transfer to be to the system, the increase of entropy principle for a reacting or nonreacting system was expressed in Chapter 7 as

$$dS_{\text{sys}} \geq \frac{\delta Q}{T} \quad (16-1)$$

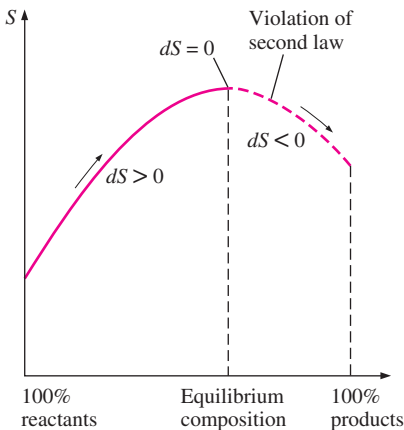


FIGURE 16-2

Equilibrium criteria for a chemical reaction that takes place adiabatically.

A system and its surroundings form an adiabatic system, and for such systems Eq. 16-1 reduces to  $dS_{\text{sys}} \geq 0$ . That is, a chemical reaction in an adiabatic chamber proceeds in the direction of increasing entropy. When the entropy reaches a maximum, the reaction stops (Fig. 16-2). Therefore, entropy is a very useful property in the analysis of reacting adiabatic systems.

When a reacting system involves heat transfer, the increase of entropy principle relation (Eq. 16-1) becomes impractical to use, however, since it requires a knowledge of heat transfer between the system and its surroundings. A more practical approach would be to develop a relation for the equilibrium criterion in terms of the properties of the reacting system only. Such a relation is developed below.

Consider a reacting (or nonreacting) simple compressible system of fixed mass with only quasi-equilibrium work modes at a specified temperature  $T$  and pressure  $P$  (Fig. 16-3). Combining the first- and the second-law relations for this system gives

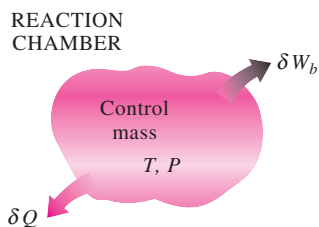


FIGURE 16-3

A control mass undergoing a chemical reaction at a specified temperature and pressure.

$$\left. \begin{aligned} \delta Q - P dV &= dU \\ dS &\geq \frac{\delta Q}{T} \end{aligned} \right\} dU + P dV - T ds \leq 0 \quad (16-2)$$

The differential of the Gibbs function ( $G = H - TS$ ) at constant temperature and pressure is

$$\begin{aligned}(dG)_{T,P} &= dH - T dS - S dT \\ &= (dU + P dV + V dP) - T dS - S dT \\ &= dU + P dV - T dS\end{aligned}\quad (16-3)$$

From Eqs. 16-2 and 16-3, we have  $(dG)_{T,P} \leq 0$ . Therefore, a chemical reaction at a specified temperature and pressure proceeds in the direction of a decreasing Gibbs function. The reaction stops and chemical equilibrium is established when the Gibbs function attains a minimum value (Fig. 16-4). Therefore, the criterion for chemical equilibrium can be expressed as

$$(dG)_{T,P} = 0 \quad (16-4)$$

A chemical reaction at a specified temperature and pressure cannot proceed in the direction of the increasing Gibbs function since this will be a violation of the second law of thermodynamics. Notice that if the temperature or the pressure is changed, the reacting system will assume a different equilibrium state, which is the state of the minimum Gibbs function at the new temperature or pressure.

To obtain a relation for chemical equilibrium in terms of the properties of the individual components, consider a mixture of four chemical components  $A$ ,  $B$ ,  $C$ , and  $D$  that exist in equilibrium at a specified temperature and pressure. Let the number of moles of the respective components be  $N_A$ ,  $N_B$ ,  $N_C$ , and  $N_D$ . Now consider a reaction that occurs to an infinitesimal extent during which differential amounts of  $A$  and  $B$  (reactants) are converted to  $C$  and  $D$  (products) while the temperature and the pressure remain constant (Fig. 16-5):



The equilibrium criterion (Eq. 16-4) requires that the change in the Gibbs function of the mixture during this process be equal to zero. That is,

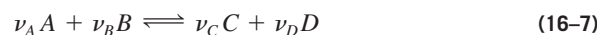
$$(dG)_{T,P} = \sum (dG_i)_{T,P} = \sum (\bar{g}_i dN_i)_{T,P} = 0 \quad (16-5)$$

or

$$\bar{g}_C dN_C + \bar{g}_D dN_D + \bar{g}_A dN_A + \bar{g}_B dN_B = 0 \quad (16-6)$$

where the  $\bar{g}$ 's are the molar Gibbs functions (also called the *chemical potentials*) at the specified temperature and pressure and the  $dN$ 's are the differential changes in the number of moles of the components.

To find a relation between the  $dN$ 's, we write the corresponding stoichiometric (theoretical) reaction



where the  $\nu$ 's are the stoichiometric coefficients, which are evaluated easily once the reaction is specified. The stoichiometric reaction plays an important role in the determination of the equilibrium composition of the reacting

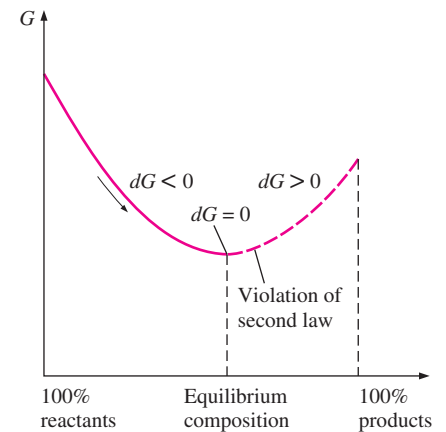


FIGURE 16-4

Criteria for chemical equilibrium for a fixed mass at a specified temperature and pressure.

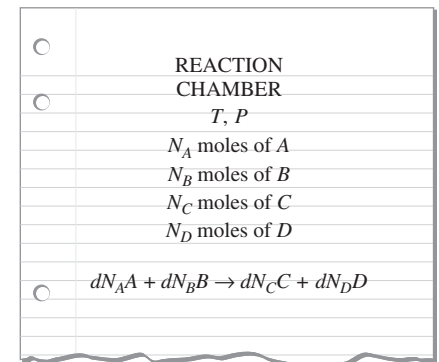


FIGURE 16-5

An infinitesimal reaction in a chamber at constant temperature and pressure.

<input type="radio"/>	
<input type="radio"/>	$\text{H}_2 \rightarrow 2\text{H}$
	$0.1\text{H}_2 \rightarrow 0.2\text{H}$
	$0.01\text{H}_2 \rightarrow 0.02\text{H}$
	$0.001\text{H}_2 \rightarrow 0.002\text{H}$
	$\nu_{\text{H}_2} = 1$
<input type="radio"/>	$\nu_{\text{H}} = 2$

FIGURE 16-6

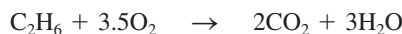
The changes in the number of moles of the components during a chemical reaction are proportional to the stoichiometric coefficients regardless of the extent of the reaction.

mixtures because the changes in the number of moles of the components are proportional to the stoichiometric coefficients (Fig. 16–6). That is,

$$\begin{aligned} dN_A &= -\varepsilon\nu_A & dN_C &= \varepsilon\nu_C \\ dN_B &= -\varepsilon\nu_B & dN_D &= \varepsilon\nu_D \end{aligned} \quad (16-8)$$

where  $\varepsilon$  is the proportionality constant and represents the extent of a reaction. A minus sign is added to the first two terms because the number of moles of the reactants  $A$  and  $B$  decreases as the reaction progresses.

For example, if the reactants are  $\text{C}_2\text{H}_6$  and  $\text{O}_2$  and the products are  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , the reaction of  $1 \mu\text{mol}$  ( $10^{-6}$  mol) of  $\text{C}_2\text{H}_6$  results in a  $2\text{-}\mu\text{mol}$  increase in  $\text{CO}_2$ , a  $3\text{-}\mu\text{mol}$  increase in  $\text{H}_2\text{O}$ , and a  $3.5\text{-}\mu\text{mol}$  decrease in  $\text{O}_2$  in accordance with the stoichiometric equation



That is, the change in the number of moles of a component is one-millionth ( $\varepsilon = 10^{-6}$ ) of the stoichiometric coefficient of that component in this case.

Substituting the relations in Eq. 16–8 into Eq. 16–6 and canceling  $\varepsilon$ , we obtain

$$\nu_C \bar{g}_C + \nu_D \bar{g}_D - \nu_A \bar{g}_A - \nu_B \bar{g}_B = 0 \quad (16-9)$$

This equation involves the stoichiometric coefficients and the molar Gibbs functions of the reactants and the products, and it is known as the **criterion for chemical equilibrium**. It is valid for any chemical reaction regardless of the phases involved.

Equation 16–9 is developed for a chemical reaction that involves two reactants and two products for simplicity, but it can easily be modified to handle chemical reactions with any number of reactants and products. Next we analyze the equilibrium criterion for ideal-gas mixtures.

## 16-2 ■ THE EQUILIBRIUM CONSTANT FOR IDEAL-GAS MIXTURES

Consider a mixture of ideal gases that exists in equilibrium at a specified temperature and pressure. Like entropy, the Gibbs function of an ideal gas depends on both the temperature and the pressure. The Gibbs function values are usually listed versus temperature at a fixed reference pressure  $P_0$ , which is taken to be 1 atm. The variation of the Gibbs function of an ideal gas with pressure at a fixed temperature is determined by using the definition of the Gibbs function ( $\bar{g} = \bar{h} - T\bar{s}$ ) and the entropy-change relation for isothermal processes [ $\Delta \bar{s} = -R_u \ln(P_2/P_1)$ ]. It yields

$$(\Delta \bar{g})_T = \Delta \bar{h} - T(\Delta \bar{s})_T = -T(\Delta \bar{s})_T = R_u T \ln \frac{P_2}{P_1}$$

Thus the Gibbs function of component  $i$  of an ideal-gas mixture at its partial pressure  $P_i$  and mixture temperature  $T$  can be expressed as

$$\bar{g}_i(T, P_i) = \bar{g}_i^*(T) + R_u T \ln P_i \quad (16-10)$$

where  $\bar{g}_i^*(T)$  represents the Gibbs function of component  $i$  at 1 atm pressure and temperature  $T$ , and  $P_i$  represents the partial pressure of component  $i$  in atmospheres. Substituting the Gibbs function expression for each component into Eq. 16–9, we obtain

$$\nu_C[\bar{g}_C^*(T) + R_u T \ln P_C] + \nu_D[\bar{g}_D^*(T) + R_u T \ln P_D] - \nu_A[\bar{g}_A^*(T) + R_u T \ln P_A] - \nu_B[\bar{g}_B^*(T) + R_u T \ln P_B] = 0$$

For convenience, we define the **standard-state Gibbs function change** as

$$\Delta G^*(T) = \nu_C \bar{g}_C^*(T) + \nu_D \bar{g}_D^*(T) - \nu_A \bar{g}_A^*(T) - \nu_B \bar{g}_B^*(T) \quad (16-11)$$

Substituting, we get

$$\Delta G^*(T) = -R_u T (\nu_C \ln P_C + \nu_D \ln P_D - \nu_A \ln P_A - \nu_B \ln P_B) = -R_u T \ln \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}} \quad (16-12)$$

Now we define the **equilibrium constant**  $K_P$  for the chemical equilibrium of ideal-gas mixtures as

$$K_P = \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}} \quad (16-13)$$

Substituting into Eq. 16–12 and rearranging, we obtain

$$K_P = e^{-\Delta G^*(T)/R_u T} \quad (16-14)$$

Therefore, the equilibrium constant  $K_P$  of an ideal-gas mixture at a specified temperature can be determined from a knowledge of the standard-state Gibbs function change at the same temperature. The  $K_P$  values for several reactions are given in Table A–28.

Once the equilibrium constant is available, it can be used to determine the equilibrium composition of reacting ideal-gas mixtures. This is accomplished by expressing the partial pressures of the components in terms of their mole fractions:

$$P_i = y_i P = \frac{N_i}{N_{\text{total}}} P$$

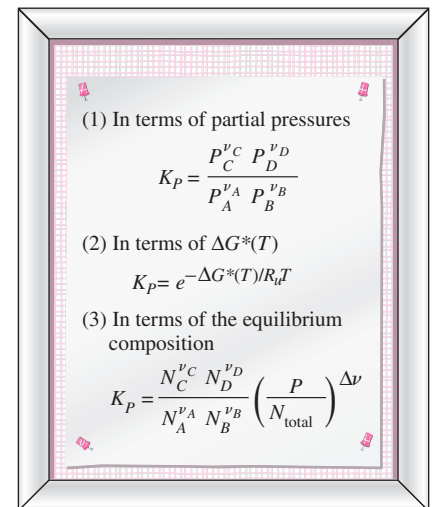
where  $P$  is the total pressure and  $N_{\text{total}}$  is the total number of moles present in the reaction chamber, including any *inert gases*. Replacing the partial pressures in Eq. 16–13 by the above relation and rearranging, we obtain (Fig. 16–7)

$$K_P = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left( \frac{P}{N_{\text{total}}} \right)^{\Delta \nu} \quad (16-15)$$

where

$$\Delta \nu = \nu_C + \nu_D - \nu_A - \nu_B$$

Equation 16–15 is written for a reaction involving two reactants and two products, but it can be extended to reactions involving any number of reactants and products.



**FIGURE 16–7**

Three equivalent  $K_P$  relations for reacting ideal-gas mixtures.

**EXAMPLE 16–1** Equilibrium Constant of a Dissociation Process

Using Eq. 16–14 and the Gibbs function data, determine the equilibrium constant  $K_p$  for the dissociation process  $\text{N}_2 \rightarrow 2\text{N}$  at  $25^\circ\text{C}$ . Compare your result to the  $K_p$  value listed in Table A–28.

**Solution** The equilibrium constant of the reaction  $\text{N}_2 \rightarrow 2\text{N}$  is listed in Table A–28 at different temperatures. It is to be verified using Gibbs function data.

**Assumptions** **1** The constituents of the mixture are ideal gases. **2** The equilibrium mixture consists of  $\text{N}_2$  and  $\text{N}$  only.

**Properties** The equilibrium constant of this reaction at 298 K is  $\ln K_p = -367.5$  (Table A–28). The Gibbs function of formation at  $25^\circ\text{C}$  and 1 atm is 0 for  $\text{N}_2$  and 455,510 kJ/kmol for  $\text{N}$  (Table A–26).

**Analysis** In the absence of  $K_p$  tables,  $K_p$  can be determined from the Gibbs function data and Eq. 16–14,

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

where, from Eq. 16–11,

$$\begin{aligned}\Delta G^*(T) &= \nu_{\text{N}} \bar{g}_{\text{N}}^*(T) - \nu_{\text{N}_2} \bar{g}_{\text{N}_2}^*(T) \\ &= (2)(455,510 \text{ kJ/kmol}) - 0 \\ &= 911,020 \text{ kJ/kmol}\end{aligned}$$

Substituting, we find

$$\begin{aligned}\ln K_p &= -\frac{911,020 \text{ kJ/kmol}}{(8.314 \text{ kJ/kmol} \cdot \text{K})(298.15 \text{ K})} \\ &= -367.5\end{aligned}$$

or

$$K_p \cong 2 \times 10^{-160}$$

The calculated  $K_p$  value is in agreement with the value listed in Table A–28. The  $K_p$  value for this reaction is practically zero, indicating that this reaction will not occur at this temperature.

**Discussion** Note that this reaction involves one product ( $\text{N}$ ) and one reactant ( $\text{N}_2$ ), and the stoichiometric coefficients for this reaction are  $\nu_{\text{N}} = 2$  and  $\nu_{\text{N}_2} = 1$ . Also note that the Gibbs function of all stable elements (such as  $\text{N}_2$ ) is assigned a value of zero at the standard reference state of  $25^\circ\text{C}$  and 1 atm. The Gibbs function values at other temperatures can be calculated from the enthalpy and absolute entropy data by using the definition of the Gibbs function,  $\bar{g}^*(T) = \bar{h}(T) - T \bar{s}^*(T)$ , where  $\bar{h}(T) = \bar{h}_f^* + \bar{h}_T - \bar{h}_{298 \text{ K}}$ .

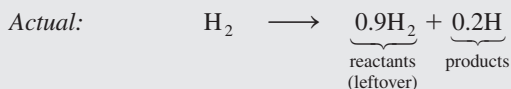
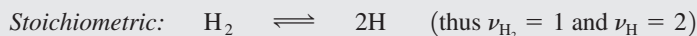
**EXAMPLE 16–2** Dissociation Temperature of Hydrogen

Determine the temperature at which 10 percent of diatomic hydrogen ( $\text{H}_2$ ) dissociates into monatomic hydrogen ( $\text{H}$ ) at a pressure of 10 atm.

**Solution** The temperature at which 10 percent of  $\text{H}_2$  dissociates into  $2\text{H}$  is to be determined.

**Assumptions** **1** The constituents of the mixture are ideal gases. **2** The equilibrium mixture consists of  $\text{H}_2$  and  $\text{H}$  only.

**Analysis** This is a dissociation process that is significant at very high temperatures only. For simplicity we consider 1 kmol of  $H_2$ , as shown in Fig. 16–8. The stoichiometric and actual reactions in this case are as follows:



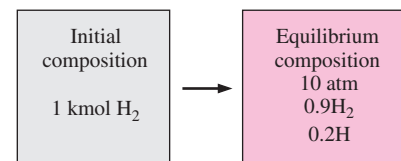
A double-headed arrow is used for the stoichiometric reaction to differentiate it from the actual reaction. This reaction involves one reactant ( $H_2$ ) and one product ( $H$ ). The equilibrium composition consists of 0.9 kmol of  $H_2$  (the leftover reactant) and 0.2 kmol of  $H$  (the newly formed product). Therefore,  $N_{H_2} = 0.9$  and  $N_H = 0.2$  and the equilibrium constant  $K_p$  is determined from Eq. 16–15 to be

$$K_p = \frac{N_H^{\nu_H}}{N_{H_2}^{\nu_{H_2}}} \left( \frac{P}{N_{\text{total}}} \right)^{\nu_H - \nu_{H_2}} = \frac{(0.2)^2}{0.9} \left( \frac{10}{0.9 + 0.2} \right)^{2-1} = 0.404$$

From Table A–28, the temperature corresponding to this  $K_p$  value is

$$T = 3535 \text{ K}$$

**Discussion** We conclude that 10 percent of  $H_2$  dissociates into  $H$  when the temperature is raised to 3535 K. If the temperature is increased further, the percentage of  $H_2$  that dissociates into  $H$  will also increase.



**FIGURE 16–8**  
Schematic for Example 16–2.

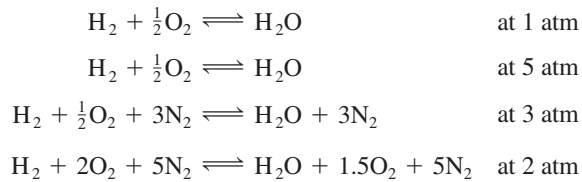
A double arrow is used in equilibrium equations as an indication that a chemical reaction does not stop when chemical equilibrium is established; rather, it proceeds in both directions at the same rate. That is, at equilibrium, the reactants are depleted at exactly the same rate as they are replenished from the products by the reverse reaction.

### 16–3 ■ SOME REMARKS ABOUT THE $K_p$ OF IDEAL-GAS MIXTURES

In the last section we developed three equivalent expressions for the equilibrium constant  $K_p$  of reacting ideal-gas mixtures: Eq. 16–13, which expresses  $K_p$  in terms of *partial pressures*; Eq. 16–14, which expresses  $K_p$  in terms of the *standard-state Gibbs function change*  $\Delta G^*(T)$ ; and Eq. 16–15, which expresses  $K_p$  in terms of the *number of moles* of the components. All three relations are equivalent, but sometimes one is more convenient to use than the others. For example, Eq. 16–15 is best suited for determining the equilibrium composition of a reacting ideal-gas mixture at a specified temperature and pressure. On the basis of these relations, we may draw the following conclusions about the equilibrium constant  $K_p$  of ideal-gas mixtures:

1. *The  $K_p$  of a reaction depends on temperature only.* It is independent of the pressure of the equilibrium mixture and is not affected by the presence of inert gases. This is because  $K_p$  depends on  $\Delta G^*(T)$ , which depends on

temperature only, and the  $\Delta G^*(T)$  of inert gases is zero (see Eq. 16–14). Thus, at a specified temperature the following four reactions have the same  $K_p$  value:



2. The  $K_p$  of the reverse reaction is  $1/K_p$ . This is easily seen from Eq. 16–13. For reverse reactions, the products and reactants switch places, and thus the terms in the numerator move to the denominator and vice versa. Consequently, the equilibrium constant of the reverse reaction becomes  $1/K_p$ . For example, from Table A–28,

$$\begin{aligned} K_p &= 0.1147 \times 10^{11} && \text{for } \text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O} && \text{at 1000 K} \\ K_p &= 8.718 \times 10^{-11} && \text{for } \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2 && \text{at 1000 K} \end{aligned}$$

3. The larger the  $K_p$ , the more complete the reaction. This is also apparent from Fig. 16–9 and Eq. 16–13. If the equilibrium composition consists largely of product gases, the partial pressures of the products ( $P_C$  and  $P_D$ ) are considerably larger than the partial pressures of the reactants ( $P_A$  and  $P_B$ ), which results in a large value of  $K_p$ . In the limiting case of a complete reaction (no leftover reactants in the equilibrium mixture),  $K_p$  approaches infinity. Conversely, very small values of  $K_p$  indicate that a reaction does not proceed to any appreciable degree. Thus reactions with very small  $K_p$  values at a specified temperature can be neglected.

A reaction with  $K_p > 1000$  (or  $\ln K_p > 7$ ) is usually assumed to proceed to completion, and a reaction with  $K_p < 0.001$  (or  $\ln K_p < -7$ ) is assumed not to occur at all. For example,  $\ln K_p = -6.8$  for the reaction  $\text{N}_2 \rightleftharpoons 2\text{N}$  at 5000 K. Therefore, the dissociation of  $\text{N}_2$  into monatomic nitrogen (N) can be disregarded at temperatures below 5000 K.

4. The mixture pressure affects the equilibrium composition (although it does not affect the equilibrium constant  $K_p$ ). This can be seen from Eq. 16–15, which involves the term  $P^{\Delta\nu}$ , where  $\Delta\nu = \sum \nu_P - \sum \nu_R$  (the difference between the number of moles of products and the number of moles of reactants in the stoichiometric reaction). At a specified temperature, the  $K_p$  value of the reaction, and thus the right-hand side of Eq. 16–15, remains constant. Therefore, the mole numbers of the reactants and the products must change to counteract any changes in the pressure term. The direction of the change depends on the sign of  $\Delta\nu$ . An increase in pressure at a specified temperature increases the number of moles of the reactants and decreases the number of moles of products if  $\Delta\nu$  is positive, have the opposite effect if  $\Delta\nu$  is negative, and have no effect if  $\Delta\nu$  is zero.

5. The presence of inert gases affects the equilibrium composition (although it does not affect the equilibrium constant  $K_p$ ). This can be seen from Eq. 16–15, which involves the term  $(1/N_{\text{total}})^{\Delta\nu}$ , where  $N_{\text{total}}$  is the total number of moles of the ideal-gas mixture at equilibrium, including inert gases. The sign of  $\Delta\nu$  determines how the presence of inert gases influences the equilibrium composition (Fig. 16–10). An increase in the number of moles of inert gases at a specified temperature and pressure decreases the number of

H <sub>2</sub> → 2H		
P = 1 atm		
T, K	K <sub>p</sub>	% mol H
1000	5.17 × 10 <sup>-18</sup>	0.00
2000	2.65 × 10 <sup>-6</sup>	0.16
3000	0.025	14.63
4000	2.545	76.80
5000	41.47	97.70
6000	267.7	99.63

FIGURE 16–9

The larger the  $K_p$ , the more complete the reaction.

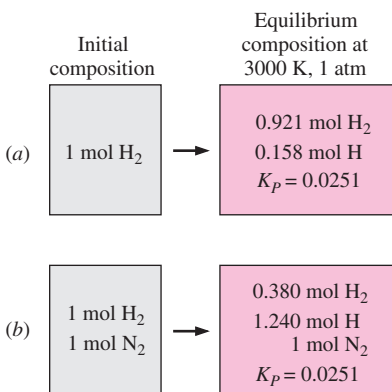


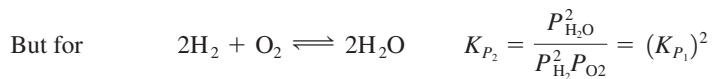
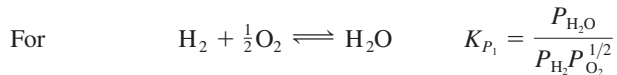
FIGURE 16–10

The presence of inert gases does not affect the equilibrium constant, but it does affect the equilibrium composition.



moles of the reactants and increases the number of moles of products if  $\Delta\nu$  is positive, have the opposite effect if  $\Delta\nu$  is negative, and have no effect if  $\Delta\nu$  is zero.

6. When the stoichiometric coefficients are doubled, the value of  $K_p$  is squared. Therefore, when one is using  $K_p$  values from a table, the stoichiometric coefficients (the  $\nu$ 's) used in a reaction must be exactly the same ones appearing in the table from which the  $K_p$  values are selected. Multiplying all the coefficients of a stoichiometric equation does not affect the mass balance, but it does affect the equilibrium constant calculations since the stoichiometric coefficients appear as exponents of partial pressures in Eq. 16–13. For example,



7. Free electrons in the equilibrium composition can be treated as an ideal gas. At high temperatures (usually above 2500 K), gas molecules start to dissociate into unattached atoms (such as  $\text{H}_2 \rightleftharpoons 2\text{H}$ ), and at even higher temperatures atoms start to lose electrons and ionize, for example,



The dissociation and ionization effects are more pronounced at low pressures. Ionization occurs to an appreciable extent only at very high temperatures, and the mixture of electrons, ions, and neutral atoms can be treated as an ideal gas. Therefore, the equilibrium composition of ionized gas mixtures can be determined from Eq. 16–15 (Fig. 16–11). This treatment may not be adequate in the presence of strong electric fields, however, since the electrons may be at a different temperature than the ions in this case.

8. Equilibrium calculations provide information on the equilibrium composition of a reaction, not on the reaction rate. Sometimes it may even take years to achieve the indicated equilibrium composition. For example, the equilibrium constant of the reaction  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$  at 298 K is about  $10^{40}$ , which suggests that a stoichiometric mixture of  $\text{H}_2$  and  $\text{O}_2$  at room temperature should react to form  $\text{H}_2\text{O}$ , and the reaction should go to completion. However, the rate of this reaction is so slow that it practically does not occur. But when the right catalyst is used, the reaction goes to completion rather quickly to the predicted value.

### EXAMPLE 16–3 Equilibrium Composition at a Specified Temperature

A mixture of 2 kmol of CO and 3 kmol of  $\text{O}_2$  is heated to 2600 K at a pressure of 304 kPa. Determine the equilibrium composition, assuming the mixture consists of  $\text{CO}_2$ , CO, and  $\text{O}_2$  (Fig. 16–12).

**Solution** A reactive gas mixture is heated to a high temperature. The equilibrium composition at that temperature is to be determined.

<input type="radio"/>	
<input type="radio"/>	$\text{H} \rightarrow \text{H}^+ + e^-$
	$K_p = \frac{N_{\text{H}^+}^{\nu_{\text{H}^+}} N_{e^-}^{\nu_{e^-}}}{N_{\text{H}}^{\nu_{\text{H}}}} \left( \frac{P}{N_{\text{total}}} \right)^{\Delta\nu}$
	where
<input type="radio"/>	$N_{\text{total}} = N_{\text{H}} + N_{\text{H}^+} + N_{e^-}$
	$\Delta\nu = \nu_{\text{H}^+} + \nu_{e^-} - \nu_{\text{H}}$
	$= 1 + 1 - 1$
	$= 1$
<input type="radio"/>	
<input type="radio"/>	

FIGURE 16–11

Equilibrium-constant relation for the ionization reaction of hydrogen.

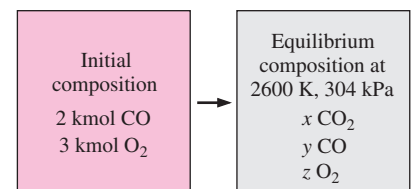
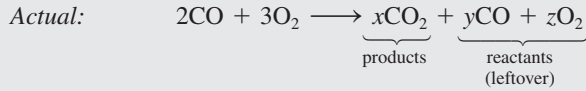
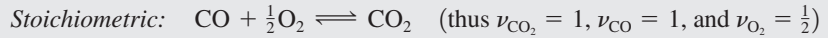


FIGURE 16–12

Schematic for Example 16–3.

**Assumptions** 1 The equilibrium composition consists of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$ .  
2 The constituents of the mixture are ideal gases.

**Analysis** The stoichiometric and actual reactions in this case are as follows:



*C balance:*  $2 = x + y$  or  $y = 2 - x$

*O balance:*  $8 = 2x + y + 2z$  or  $z = 3 - \frac{x}{2}$

*Total number of moles:*  $N_{\text{total}} = x + y + z = 5 - \frac{x}{2}$

*Pressure:*  $P = 304 \text{ kPa} = 3.0 \text{ atm}$

The closest reaction listed in Table A-28 is  $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$ , for which  $\ln K_p = -2.801$  at 2600 K. The reaction we have is the inverse of this, and thus  $\ln K_p = +2.801$ , or  $K_p = 16.461$  in our case.

Assuming ideal-gas behavior for all components, the equilibrium constant relation (Eq. 16-15) becomes

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

Substituting, we get

$$16.461 = \frac{x}{(2-x)(3-x/2)^{1/2}} \left( \frac{3}{5-x/2} \right)^{-1/2}$$

Solving for  $x$  yields

$$x = 1.906$$

Then

$$y = 2 - x = 0.094$$

$$z = 3 - \frac{x}{2} = 2.047$$

Therefore, the equilibrium composition of the mixture at 2600 K and 304 kPa is



**Discussion** In solving this problem, we disregarded the dissociation of  $\text{O}_2$  into  $\text{O}$  according to the reaction  $\text{O}_2 \rightarrow 2\text{O}$ , which is a real possibility at high temperatures. This is because  $\ln K_p = -7.521$  at 2600 K for this reaction, which indicates that the amount of  $\text{O}_2$  that dissociates into  $\text{O}$  is negligible. (Besides, we have not learned how to deal with simultaneous reactions yet. We will do so in the next section.)

**EXAMPLE 16-4** Effect of Inert Gases on Equilibrium Composition

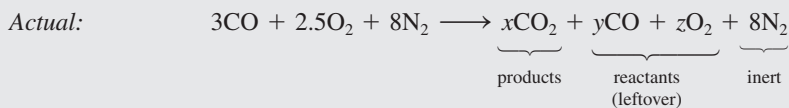
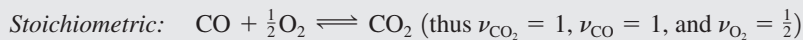
A mixture of 3 kmol of CO, 2.5 kmol of O<sub>2</sub>, and 8 kmol of N<sub>2</sub> is heated to 2600 K at a pressure of 5 atm. Determine the equilibrium composition of the mixture (Fig. 16-13).

**Solution** A gas mixture is heated to a high temperature. The equilibrium composition at the specified temperature is to be determined.

**Assumptions** 1 The equilibrium composition consists of CO<sub>2</sub>, CO, O<sub>2</sub>, and N<sub>2</sub>. 2 The constituents of the mixture are ideal gases.

**Analysis** This problem is similar to Example 16-3, except that it involves an inert gas N<sub>2</sub>. At 2600 K, some possible reactions are O<sub>2</sub> ⇌ 2O (ln K<sub>P</sub> = -7.521), N<sub>2</sub> ⇌ 2N (ln K<sub>P</sub> = -28.304),  $\frac{1}{2}$ O<sub>2</sub> +  $\frac{1}{2}$ N<sub>2</sub> ⇌ NO (ln K<sub>P</sub> = -2.671), and CO +  $\frac{1}{2}$ O<sub>2</sub> ⇌ CO<sub>2</sub> (ln K<sub>P</sub> = 2.801 or K<sub>P</sub> = 16.461). Based on these K<sub>P</sub> values, we conclude that the O<sub>2</sub> and N<sub>2</sub> will not dissociate to any appreciable degree, but a small amount will combine to form some oxides of nitrogen. (We disregard the oxides of nitrogen in this example, but they should be considered in a more refined analysis.) We also conclude that most of the CO will combine with O<sub>2</sub> to form CO<sub>2</sub>. Notice that despite the changes in pressure, the number of moles of CO and O<sub>2</sub> and the presence of an inert gas, the K<sub>P</sub> value of the reaction is the same as that used in Example 16-3.

The stoichiometric and actual reactions in this case are



*C balance:*  $3 = x + y$  or  $y = 3 - x$

*O balance:*  $8 = 2x + y + 2z$  or  $z = 2.5 - \frac{x}{2}$

*Total number of moles:*  $N_{\text{total}} = x + y + z + 8 = 13.5 - \frac{x}{2}$

Assuming ideal-gas behavior for all components, the equilibrium constant relation (Eq. 16-15) becomes

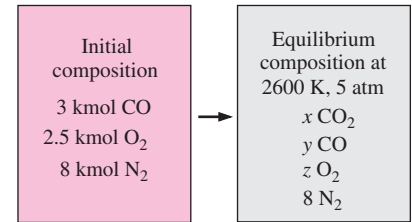
$$K_P = \frac{N_{\text{CO}_2}^{\nu_{\text{CO}_2}}}{N_{\text{CO}}^{\nu_{\text{CO}}} N_{\text{O}_2}^{\nu_{\text{O}_2}}} \left( \frac{P}{N_{\text{total}}} \right)^{\nu_{\text{CO}_2} - \nu_{\text{CO}} - \nu_{\text{O}_2}}$$

Substituting, we get

$$16.461 = \frac{x}{(3-x)(2.5-x/2)^{1/2}} \left( \frac{5}{13.5-x/2} \right)^{-1/2}$$

Solving for  $x$  yields

$$x = 2.754$$



**FIGURE 16-13**

Schematic for Example 16-4.

Then

$$y = 3 - x = 0.246$$

$$z = 2.5 - \frac{x}{2} = 1.123$$

Therefore, the equilibrium composition of the mixture at 2600 K and 5 atm is



**Discussion** Note that the inert gases do not affect the  $K_p$  value or the  $K_p$  relation for a reaction, but they do affect the equilibrium composition.

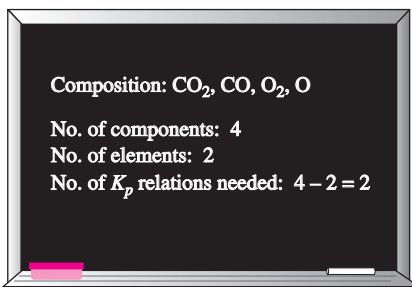
## 16-4 ■ CHEMICAL EQUILIBRIUM FOR SIMULTANEOUS REACTIONS

The reacting mixtures we have considered so far involved only one reaction, and writing a  $K_p$  relation for that reaction was sufficient to determine the equilibrium composition of the mixture. However, most practical chemical reactions involve two or more reactions that occur simultaneously, which makes them more difficult to deal with. In such cases, it becomes necessary to apply the equilibrium criterion to all possible reactions that may occur in the reaction chamber. When a chemical species appears in more than one reaction, the application of the equilibrium criterion, together with the mass balance for each chemical species, results in a system of simultaneous equations from which the equilibrium composition can be determined.

We have shown earlier that a reacting system at a specified temperature and pressure achieves chemical equilibrium when its Gibbs function reaches a minimum value, that is,  $(dG)_{T,P} = 0$ . This is true regardless of the number of reactions that may be occurring. When two or more reactions are involved, this condition is satisfied only when  $(dG)_{T,P} = 0$  for each reaction. Assuming ideal-gas behavior, the  $K_p$  of each reaction can be determined from Eq. 16-15, with  $N_{\text{total}}$  being the total number of moles present in the equilibrium mixture.

The determination of the equilibrium composition of a reacting mixture requires that we have as many equations as unknowns, where the unknowns are the number of moles of each chemical species present in the equilibrium mixture. The mass balance of each element involved provides one equation. The rest of the equations must come from the  $K_p$  relations written for each reaction. Thus we conclude that *the number of  $K_p$  relations needed to determine the equilibrium composition of a reacting mixture is equal to the number of chemical species minus the number of elements present in equilibrium*. For an equilibrium mixture that consists of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{O}_2$ , and  $\text{O}$ , for example, two  $K_p$  relations are needed to determine the equilibrium composition since it involves four chemical species and two elements (Fig. 16-14).

The determination of the equilibrium composition of a reacting mixture in the presence of two simultaneous reactions is here with an example.



**FIGURE 16-14**

The number of  $K_p$  relations needed to determine the equilibrium composition of a reacting mixture is the difference between the number of species and the number of elements.

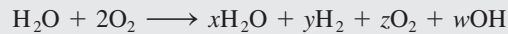
### EXAMPLE 16-5 Equilibrium Composition for Simultaneous Reactions

A mixture of 1 kmol of  $\text{H}_2\text{O}$  and 2 kmol of  $\text{O}_2$  is heated to 4000 K at a pressure of 1 atm. Determine the equilibrium composition of this mixture, assuming that only  $\text{H}_2\text{O}$ ,  $\text{OH}$ ,  $\text{O}_2$ , and  $\text{H}_2$  are present (Fig. 16–15).

**Solution** A gas mixture is heated to a specified temperature at a specified pressure. The equilibrium composition is to be determined.

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

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

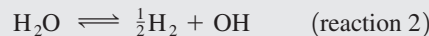
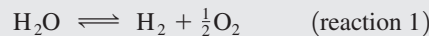


Mass balances for hydrogen and oxygen yield

$$H \text{ balance:} \quad 2 = 2x + 2y + w \quad (1)$$

$$O \text{ balance:} \quad 5 = x + 2z + w \quad (2)$$

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. It appears that part of the  $\text{H}_2\text{O}$  in the products is dissociated into  $\text{H}_2$  and  $\text{OH}$  during this process, according to the stoichiometric reactions



The equilibrium constants for these two reactions at 4000 K are determined from Table A–28 to be

$$\ln K_{p_1} = -0.542 \longrightarrow K_{p_1} = 0.5816$$

$$\ln K_{p_2} = -0.044 \longrightarrow K_{p_2} = 0.9570$$

The  $K_p$  relations for these two simultaneous reactions are

$$K_{p_1} = \frac{N_{\text{H}_2}^{\nu_{\text{H}_2}} N_{\text{O}_2}^{\nu_{\text{O}_2}}}{N_{\text{H}_2\text{O}}^{\nu_{\text{H}_2\text{O}}}} \left( \frac{P}{N_{\text{total}}} \right)^{\nu_{\text{H}_2} + \nu_{\text{O}_2} - \nu_{\text{H}_2\text{O}}}$$

$$K_{p_2} = \frac{N_{\text{H}_2}^{\nu_{\text{H}_2}} N_{\text{OH}}^{\nu_{\text{OH}}}}{N_{\text{H}_2\text{O}}^{\nu_{\text{H}_2\text{O}}}} \left( \frac{P}{N_{\text{total}}} \right)^{\nu_{\text{H}_2} + \nu_{\text{OH}} - \nu_{\text{H}_2\text{O}}}$$

where

$$N_{\text{total}} = N_{\text{H}_2\text{O}} + N_{\text{H}_2} + N_{\text{O}_2} + N_{\text{OH}} = x + y + z + w$$

Substituting yields

$$0.5816 = \frac{(y)(z)^{1/2}}{x} \left( \frac{1}{x + y + z + w} \right)^{1/2} \quad (3)$$

$$0.9570 = \frac{(w)(y)^{1/2}}{x} \left( \frac{1}{x + y + z + w} \right)^{1/2} \quad (4)$$

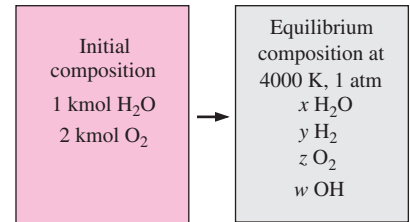


FIGURE 16-15

Schematic for Example 16–5.

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

$$\begin{aligned}x &= 0.271 & y &= 0.213 \\z &= 1.849 & w &= 1.032\end{aligned}$$

Therefore, the equilibrium composition of 1 kmol  $\text{H}_2\text{O}$  and 2 kmol  $\text{O}_2$  at 1 atm and 4000 K is



**Discussion** We could also solve this problem by using the  $K_p$  relation for the stoichiometric reaction  $\text{O}_2 \rightleftharpoons 2\text{O}$  as one of the two equations.

Solving a system of simultaneous nonlinear equations is extremely tedious and time-consuming if it is done by hand. Thus it is often necessary to solve these kinds of problems by using an equation solver such as EES.

## 16-5 ■ VARIATION OF $K_p$ WITH TEMPERATURE

It was shown in Section 16-2 that the equilibrium constant  $K_p$  of an ideal gas depends on temperature only, and it is related to the standard-state Gibbs function change  $\Delta G^*(T)$  through the relation (Eq. 16-14)

$$\ln K_p = -\frac{\Delta G^*(T)}{R_u T}$$

In this section we develop a relation for the variation of  $K_p$  with temperature in terms of other properties.

Substituting  $\Delta G^*(T) = \Delta H^*(T) - T \Delta S^*(T)$  into the above relation and differentiating with respect to temperature, we get

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H^*(T)}{R_u T^2} - \frac{d[\Delta H^*(T)]}{R_u T dT} + \frac{d[\Delta S^*(T)]}{R_u dT}$$

At constant pressure, the second  $T ds$  relation,  $T ds = dh - v dP$ , reduces to  $T ds = dh$ . Also,  $T d(\Delta S^*) = d(\Delta H^*)$  since  $\Delta S^*$  and  $\Delta H^*$  consist of entropy and enthalpy terms of the reactants and the products. Therefore, the last two terms in the above relation cancel, and it reduces to

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H^*(T)}{R_u T^2} = \frac{\bar{h}_R(T)}{R_u T^2} \quad (16-17)$$

where  $\bar{h}_R(T)$  is the enthalpy of reaction at temperature  $T$ . Notice that we dropped the superscript \* (which indicates a constant pressure of 1 atm) from  $\Delta H(T)$ , since the enthalpy of an ideal gas depends on temperature only and is independent of pressure. Equation 16-17 is an expression of the variation of  $K_p$  with temperature in terms of  $\bar{h}_R(T)$ , and it is known as the **van't Hoff equation**. To integrate it, we need to know how  $\bar{h}_R$  varies with  $T$ . For small temperature intervals,  $\bar{h}_R$  can be treated as a constant and Eq. 16-17 can be integrated to yield

$$\ln \frac{K_{p_2}}{K_{p_1}} \cong \frac{\bar{h}_R}{R_u} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (16-18)$$

This equation has two important implications. First, it provides a means of calculating the  $\bar{h}_R$  of a reaction from a knowledge of  $K_p$ , which is easier to determine. Second, it shows that exothermic reactions ( $\bar{h}_R < 0$ ) such as combustion processes are less complete at higher temperatures since  $K_p$  decreases with temperature for such reactions (Fig. 16–16).

Reaction: $C + O_2 \rightarrow CO_2$	
$T, K$	$K_p$
1000	$4.78 \times 10^{20}$
2000	$2.25 \times 10^{10}$
3000	$7.80 \times 10^6$
4000	$1.41 \times 10^5$

FIGURE 16–16

Exothermic reactions are less complete at higher temperatures.

### EXAMPLE 16–6 The Enthalpy of Reaction of a Combustion Process

Estimate the enthalpy of reaction  $\bar{h}_R$  for the combustion process of hydrogen  $H_2 + 0.5O_2 \rightarrow H_2O$  at 2000 K, using (a) enthalpy data and (b)  $K_p$  data.

**Solution** The  $\bar{h}_R$  at a specified temperature is to be determined using the enthalpy and  $K_p$  data.

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

**Analysis** (a) The  $\bar{h}_R$  of the combustion process of  $H_2$  at 2000 K is the amount of energy released as 1 kmol of  $H_2$  is burned in a steady-flow combustion chamber at a temperature of 2000 K. It can be determined from Eq. 15–6,

$$\begin{aligned}\bar{h}_R &= \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p - \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r \\ &= N_{H_2O}(\bar{h}_f^\circ + \bar{h}_{2000\text{ K}} - \bar{h}_{298\text{ K}})_{H_2O} - N_{H_2}(\bar{h}_f^\circ + \bar{h}_{2000\text{ K}} - \bar{h}_{298\text{ K}})_{H_2} \\ &\quad - N_{O_2}(\bar{h}_f^\circ + \bar{h}_{2000\text{ K}} - \bar{h}_{298\text{ K}})_{O_2}\end{aligned}$$

Substituting yields

$$\begin{aligned}\bar{h}_R &= (1 \text{ kmol } H_2O)[(-241,820 + 82,593 - 9904) \text{ kJ/kmol } H_2O] \\ &\quad - (1 \text{ kmol } H_2)[(0 + 61,400 - 8468) \text{ kJ/kmol } H_2] \\ &\quad - (0.5 \text{ kmol } O_2)[(0 + 67,881 - 8682) \text{ kJ/kmol } O_2] \\ &= \mathbf{-251,663 \text{ kJ/kmol}}\end{aligned}$$

(b) The  $\bar{h}_R$  value at 2000 K can be estimated by using  $K_p$  values at 1800 and 2200 K (the closest two temperatures to 2000 K for which  $K_p$  data are available) from Table A–28. They are  $K_{p_1} = 18,509$  at  $T_1 = 1800$  K and  $K_{p_2} = 869.6$  at  $T_2 = 2200$  K. By substituting these values into Eq. 16–18, the  $\bar{h}_R$  value is determined to be

$$\begin{aligned}\ln \frac{K_{p_2}}{K_{p_1}} &\cong \frac{\bar{h}_R}{R_u} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln \frac{869.6}{18,509} &\cong \frac{\bar{h}_R}{8.314 \text{ kJ/kmol} \cdot \text{K}} \left( \frac{1}{1800 \text{ K}} - \frac{1}{2200 \text{ K}} \right) \\ \bar{h}_R &\cong \mathbf{-251,698 \text{ kJ/kmol}}\end{aligned}$$

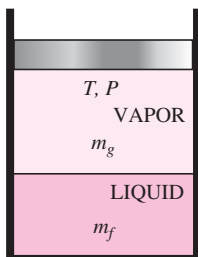
**Discussion** Despite the large temperature difference between  $T_1$  and  $T_2$  (400 K), the two results are almost identical. The agreement between the two results would be even better if a smaller temperature interval were used.



**FIGURE 16-17**

Wet clothes hung in an open area eventually dry as a result of mass transfer from the liquid phase to the vapor phase.

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**FIGURE 16-18**

A liquid–vapor mixture in equilibrium at a constant temperature and pressure.

## 16-6 ■ PHASE EQUILIBRIUM

We showed at the beginning of this chapter that the equilibrium state of a system at a specified temperature and pressure is the state of the minimum Gibbs function, and the equilibrium criterion for a reacting or nonreacting system was expressed as (Eq. 16-4)

$$(dG)_{T,P} = 0$$

In the preceding sections we applied the equilibrium criterion to reacting systems. In this section, we apply it to nonreacting multiphase systems.

We know from experience that a wet T-shirt hanging in an open area eventually dries, a small amount of water left in a glass evaporates, and the aftershave in an open bottle quickly disappears (Fig. 16-17). These examples suggest that there is a driving force between the two phases of a substance that forces the mass to transform from one phase to another. The magnitude of this force depends, among other things, on the relative concentrations of the two phases. A wet T-shirt dries much quicker in dry air than it does in humid air. In fact, it does not dry at all if the relative humidity of the environment is 100 percent. In this case, there is no transformation from the liquid phase to the vapor phase, and the two phases are in **phase equilibrium**. The conditions of phase equilibrium change, however, if the temperature or the pressure is changed. Therefore, we examine phase equilibrium at a specified temperature and pressure.

### Phase Equilibrium for a Single-Component System

The equilibrium criterion for two phases of a pure substance such as water is easily developed by considering a mixture of saturated liquid and saturated vapor in equilibrium at a specified temperature and pressure, such as that shown in Fig. 16-18. The total Gibbs function of this mixture is

$$G = m_f g_f + m_g g_g$$

where  $g_f$  and  $g_g$  are the Gibbs functions of the liquid and vapor phases per unit mass, respectively. Now imagine a disturbance during which a differential amount of liquid  $dm_f$  evaporates at constant temperature and pressure. The change in the total Gibbs function during this disturbance is

$$(dG)_{T,P} = g_f dm_f + g_g dm_g$$

since  $g_f$  and  $g_g$  remain constant at constant temperature and pressure. At equilibrium,  $(dG)_{T,P} = 0$ . Also from the conservation of mass,  $dm_g = -dm_f$ . Substituting, we obtain

$$(dG)_{T,P} = (g_f - g_g) dm_f$$

which must be equal to zero at equilibrium. It yields

$$g_f = g_g \quad (16-19)$$

Therefore, *the two phases of a pure substance are in equilibrium when each phase has the same value of specific Gibbs function*. Also, at the triple point (the state at which all three phases coexist in equilibrium), the specific Gibbs functions of all three phases are equal to each other.



What happens if  $g_f > g_g$ ? Obviously the two phases are not in equilibrium at that moment. The second law requires that  $(dG)_{T,P} = (g_f - g_g) dm_f \leq 0$ . Thus,  $dm_f$  must be negative, which means that some liquid must vaporize until  $g_f = g_g$ . Therefore, the Gibbs function difference is the driving force for phase change, just as the temperature difference is the driving force for heat transfer.

### EXAMPLE 16–7 Phase Equilibrium for a Saturated Mixture

Show that a mixture of saturated liquid water and saturated water vapor at 120°C satisfies the criterion for phase equilibrium.

**Solution** It is to be shown that a saturated mixture satisfies the criterion for phase equilibrium.

**Properties** The properties of saturated water at 120°C are  $h_f = 503.81$  kJ/kg,  $s_f = 1.5279$  kJ/kg · K,  $h_g = 2706.0$  kJ/kg, and  $s_g = 7.1292$  kJ/kg · K (Table A–4).

**Analysis** Using the definition of Gibbs function together with the enthalpy and entropy data, we have

$$\begin{aligned} g_f &= h_f - Ts_f = 503.81 \text{ kJ/kg} - (393.15 \text{ K})(1.5279 \text{ kJ/kg} \cdot \text{K}) \\ &= -96.9 \text{ kJ/kg} \end{aligned}$$

and

$$\begin{aligned} g_g &= h_g - Ts_g = 2706.0 \text{ kJ/kg} - (393.15 \text{ K})(7.1292 \text{ kJ/kg} \cdot \text{K}) \\ &= -96.8 \text{ kJ/kg} \end{aligned}$$

**Discussion** The two results are in close agreement. They would match exactly if more accurate property data were used. Therefore, the criterion for phase equilibrium is satisfied.

## The Phase Rule

Notice that a single-component two-phase system may exist in equilibrium at different temperatures (or pressures). However, once the temperature is fixed, the system is locked into an equilibrium state and all intensive properties of each phase (except their relative amounts) are fixed. Therefore, a single-component two-phase system has one independent property, which may be taken to be the temperature or the pressure.

In general, the number of independent variables associated with a multicomponent, multiphase system is given by the **Gibbs phase rule**, expressed as

$$IV = C - PH + 2 \quad (16-20)$$

where  $IV$  = the number of independent variables,  $C$  = the number of components, and  $PH$  = the number of phases present in equilibrium. For the single-component ( $C = 1$ ) two-phase ( $PH = 2$ ) system discussed above, for example, one independent intensive property needs to be specified ( $IV = 1$ , Fig. 16–19). At the triple point, however,  $PH = 3$  and thus  $IV = 0$ . That is, none of the properties of a pure substance at the triple point can be varied. Also, based on this rule, a pure substance that exists in a single phase

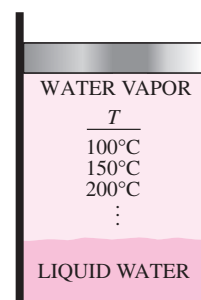


FIGURE 16–19

According to the Gibbs phase rule, a single-component, two-phase system can have only one independent variable.

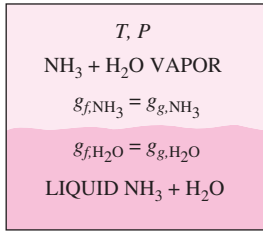


FIGURE 16–20

A multicomponent multiphase system is in phase equilibrium when the specific Gibbs function of each component is the same in all phases.

(PH = 1) has two independent variables. In other words, two independent intensive properties need to be specified to fix the equilibrium state of a pure substance in a single phase.

### Phase Equilibrium for a Multicomponent System

Many multiphase systems encountered in practice involve two or more components. A multicomponent multiphase system at a specified temperature and pressure is in phase equilibrium when there is no driving force between the different phases of each component. Thus, for phase equilibrium, the specific Gibbs function of each component must be the same in all phases (Fig. 16–20). That is,

$$g_{f,1} = g_{g,1} = g_{s,1} \quad \text{for component 1}$$

$$g_{f,2} = g_{g,2} = g_{s,2} \quad \text{for component 2}$$

.....

$$g_{f,N} = g_{g,N} = g_{s,N} \quad \text{for component } N$$

We could also derive these relations by using mathematical rigor instead of physical arguments.

Some components may exist in more than one solid phase at the specified temperature and pressure. In this case, the specific Gibbs function of each solid phase of a component must also be the same for phase equilibrium.

In this section we examine the phase equilibrium of two-component systems that involve two phases (liquid and vapor) in equilibrium. For such systems,  $C = 2$ ,  $PH = 2$ , and thus  $IV = 2$ . That is, a two-component, two-phase system has two independent variables, and such a system will not be in equilibrium unless two independent intensive properties are fixed.

In general, the two phases of a two-component system do not have the same composition in each phase. That is, the mole fraction of a component is different in different phases. This is illustrated in Fig. 16–21 for the two-phase mixture of oxygen and nitrogen at a pressure of 0.1 MPa. On this diagram, the vapor line represents the equilibrium composition of the vapor phase at various temperatures, and the liquid line does the same for the liquid phase. At 84 K, for example, the mole fractions are 30 percent nitrogen and 70 percent oxygen in the liquid phase and 66 percent nitrogen and 34 percent oxygen in the vapor phase. Notice that

$$y_{f,N_2} + y_{f,O_2} = 0.30 + 0.70 = 1 \tag{16-21a}$$

$$y_{g,N_2} + y_{g,O_2} = 0.66 + 0.34 = 1 \tag{16-21b}$$

Therefore, once the temperature and pressure (two independent variables) of a two-component, two-phase mixture are specified, the equilibrium composition of each phase can be determined from the phase diagram, which is based on experimental measurements.

It is interesting to note that temperature is a *continuous* function, but mole fraction (which is a dimensionless concentration), in general, is not. The water and air temperatures at the free surface of a lake, for example, are always the same. The mole fractions of air on the two sides of a water–air interface, however, are obviously very different (in fact, the mole fraction of air in water is close to zero). Likewise, the mole fractions of water on the

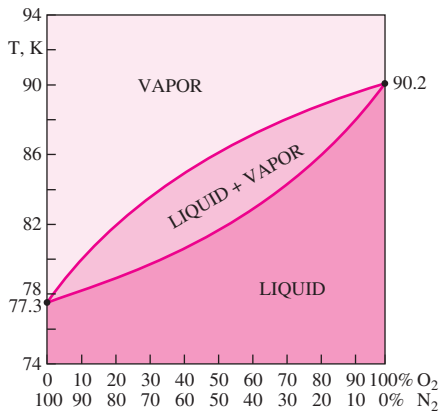


FIGURE 16–21

Equilibrium diagram for the two-phase mixture of oxygen and nitrogen at 0.1 MPa.

two sides of a water–air interface are also different even when air is saturated (Fig. 16–22). Therefore, when specifying mole fractions in two-phase mixtures, we need to clearly specify the intended phase.

In most practical applications, the two phases of a mixture are not in phase equilibrium since the establishment of phase equilibrium requires the diffusion of species from higher concentration regions to lower concentration regions, which may take a long time. However, phase equilibrium always exists at the interface of two phases of a species. In the case of air–water interface, the mole fraction of water vapor in the air is easily determined from saturation data, as shown in Example 16–8.

The situation is similar at *solid–liquid* interfaces. Again, at a given temperature, only a certain amount of solid can be dissolved in a liquid, and the solubility of the solid in the liquid is determined from the requirement that thermodynamic equilibrium exists between the solid and the solution at the interface. The **solubility** represents *the maximum amount of solid that can be dissolved in a liquid at a specified temperature* and is widely available in chemistry handbooks. In Table 16–1 we present sample solubility data for sodium chloride (NaCl) and calcium bicarbonate [ $\text{Ca}(\text{HCO}_3)_2$ ] at various temperatures. For example, the solubility of salt (NaCl) in water at 310 K is 36.5 kg per 100 kg of water. Therefore, the mass fraction of salt in the saturated brine is simply

$$\text{mf}_{\text{salt,liquid side}} = \frac{m_{\text{salt}}}{m} = \frac{36.5 \text{ kg}}{(100 + 36.5) \text{ kg}} = 0.267 \text{ (or 26.7 percent)}$$

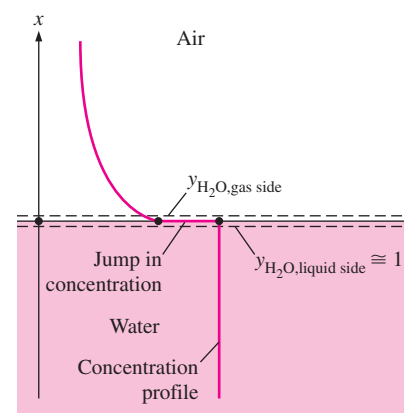
whereas the mass fraction of salt in the pure solid salt is  $\text{mf} = 1.0$ .

Many processes involve the absorption of a gas into a liquid. Most gases are weakly soluble in liquids (such as air in water), and for such dilute solutions the mole fractions of a species  $i$  in the gas and liquid phases at the interface are observed to be proportional to each other. That is,  $y_{i,\text{gas side}} \propto y_{i,\text{liquid side}}$  or  $P_{i,\text{gas side}} \propto P y_{i,\text{liquid side}}$  since  $y_i = P_i/P$  for ideal-gas mixtures. This is known as the **Henry's law** and is expressed as

$$y_{i,\text{liquid side}} = \frac{P_{i,\text{gas side}}}{H} \quad (16-22)$$

where  $H$  is the **Henry's constant**, which is the product of the total pressure of the gas mixture and the proportionality constant. For a given species, it is a function of temperature only and is practically independent of pressure for pressures under about 5 atm. Values of the Henry's constant for a number of aqueous solutions are given in Table 16–2 for various temperatures. From this table and the equation above we make the following observations:

1. The concentration of a gas dissolved in a liquid is inversely proportional to Henry's constant. Therefore, the larger the Henry's constant, the smaller the concentration of dissolved gases in the liquid.
2. The Henry's constant increases (and thus the fraction of a dissolved gas in the liquid decreases) with increasing temperature. Therefore, the dissolved gases in a liquid can be driven off by heating the liquid (Fig. 16–23).
3. The concentration of a gas dissolved in a liquid is proportional to the partial pressure of the gas. Therefore, the amount of gas dissolved in a liquid can be increased by increasing the pressure of the gas. This can be used to advantage in the carbonation of soft drinks with  $\text{CO}_2$  gas.



**FIGURE 16–22**

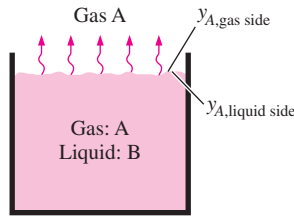
Unlike temperature, the mole fraction of species on the two sides of a liquid–gas (or solid–gas or solid–liquid) interface are usually not the same.

**TABLE 16–1**

Solubility of two inorganic compounds in water at various temperatures, in kg (in 100 kg of water)

(from *Handbook of Chemistry*, McGraw-Hill, 1961)

Temperature, K	Solute	
	Salt NaCl	Calcium bicarbonate $\text{Ca}(\text{HCO}_3)_2$
273.15	35.7	16.15
280	35.8	16.30
290	35.9	16.53
300	36.2	16.75
310	36.5	16.98
320	36.9	17.20
330	37.2	17.43
340	37.6	17.65
350	38.2	17.88
360	38.8	18.10
370	39.5	18.33
373.15	39.8	18.40



$$y_{A,\text{gas side}} \propto y_{A,\text{liquid side}}$$

or

$$\frac{P_{A,\text{gas side}}}{P} \propto y_{A,\text{liquid side}}$$

or

$$P_{A,\text{gas side}} = H y_{A,\text{liquid side}}$$

TABLE 16–2

Henry's constant  $H$  (in bars) for selected gases in water at low to moderate pressures (for gas  $i$ ,  $H = P_{i,\text{gas side}}/y_{i,\text{water side}}$ ) (from Mills, Table A.21, p. 874)

Solute	290 K	300 K	310 K	320 K	330 K	340 K
H <sub>2</sub> S	440	560	700	830	980	1140
CO <sub>2</sub>	1,280	1,710	2,170	2,720	3,220	—
O <sub>2</sub>	38,000	45,000	52,000	57,000	61,000	65,000
H <sub>2</sub>	67,000	72,000	75,000	76,000	77,000	76,000
CO	51,000	60,000	67,000	74,000	80,000	84,000
Air	62,000	74,000	84,000	92,000	99,000	104,000
N <sub>2</sub>	76,000	89,000	101,000	110,000	118,000	124,000

FIGURE 16–23

Dissolved gases in a liquid can be driven off by heating the liquid.

Strictly speaking, the result obtained from Eq. 16–22 for the mole fraction of dissolved gas is valid for the liquid layer just beneath the interface, but not necessarily the entire liquid. The latter will be the case only when thermodynamic phase equilibrium is established throughout the entire liquid body.

We mentioned earlier that the use of Henry's law is limited to dilute gas–liquid solutions, that is, liquids with a small amount of gas dissolved in them. Then the question that arises naturally is, what do we do when the gas is highly soluble in the liquid (or solid), such as ammonia in water? In this case, the linear relationship of Henry's law does not apply, and the mole fraction of a gas dissolved in the liquid (or solid) is usually expressed as a function of the partial pressure of the gas in the gas phase and the temperature. An approximate relation in this case for the *mole fractions* of a species on the *liquid* and *gas sides* of the interface is given by **Raoult's law** as

$$P_{i,\text{gas side}} = y_{i,\text{gas side}} P_{\text{total}} = y_{i,\text{liquid side}} P_{i,\text{sat}}(T) \quad (16-23)$$

where  $P_{i,\text{sat}}(T)$  is the *saturation pressure* of the species  $i$  at the interface temperature and  $P_{\text{total}}$  is the *total pressure* on the gas phase side. Tabular data are available in chemical handbooks for common solutions such as the ammonia–water solution that is widely used in absorption-refrigeration systems.

Gases may also dissolve in *solids*, but the diffusion process in this case can be very complicated. The dissolution of a gas may be independent of the structure of the solid, or it may depend strongly on its porosity. Some dissolution processes (such as the dissolution of hydrogen in titanium, similar to the dissolution of CO<sub>2</sub> in water) are *reversible*, and thus maintaining the gas content in the solid requires constant contact of the solid with a reservoir of that gas. Some other dissolution processes are *irreversible*. For example, oxygen gas dissolving in titanium forms TiO<sub>2</sub> on the surface, and the process does not reverse itself.

The molar density of the gas species  $i$  in the solid at the interface  $\bar{\rho}_{i,\text{solid side}}$  is proportional to the *partial pressure* of the species  $i$  in the gas  $P_{i,\text{gas side}}$  on the gas side of the interface and is expressed as

$$\bar{\rho}_{i,\text{solid side}} = \mathcal{S} \times P_{i,\text{gas side}} \quad (\text{kmol/m}^3) \quad (16-24)$$

where  $\mathcal{S}$  is the solubility. Expressing the pressure in bars and noting that the unit of molar concentration is kmol of species  $i$  per  $\text{m}^3$ , the unit of solubility is  $\text{kmol}/\text{m}^3 \cdot \text{bar}$ . Solubility data for selected gas–solid combinations are given in Table 16–3. The product of *solubility* of a gas and the *diffusion coefficient* of the gas in a solid is referred to as the *permeability*, which is a measure of the ability of the gas to penetrate a solid. Permeability is inversely proportional to thickness and has the unit  $\text{kmol}/\text{s} \cdot \text{m} \cdot \text{bar}$ .

Finally, if a process involves the *sublimation* of a pure solid such as ice or the *evaporation* of a pure liquid such as water in a different medium such as air, the mole (or mass) fraction of the substance in the liquid or solid phase is simply taken to be 1.0, and the partial pressure and thus the mole fraction of the substance in the gas phase can readily be determined from the saturation data of the substance at the specified temperature. Also, the assumption of thermodynamic equilibrium at the interface is very reasonable for pure solids, pure liquids, and solutions except when chemical reactions are occurring at the interface.

TABLE 16–3

Solubility of selected gases and solids (from Barrer)

(for gas  $i$ ,  $\mathcal{S} = \bar{\rho}_{i,\text{solid side}}/P_{i,\text{gas side}}$ )

$\mathcal{S}$			
Gas	Solid	$T$ K	$\text{kmol}/\text{m}^3 \cdot \text{bar}$
$\text{O}_2$	Rubber	298	0.00312
$\text{N}_2$	Rubber	298	0.00156
$\text{CO}_2$	Rubber	298	0.04015
He	$\text{SiO}_2$	298	0.00045
$\text{H}_2$	Ni	358	0.00901

### EXAMPLE 16–8 Mole Fraction of Water Vapor Just over a Lake

Determine the mole fraction of the water vapor at the surface of a lake whose temperature is  $15^\circ\text{C}$ , and compare it to the mole fraction of water in the lake (Fig. 16–24). Take the atmospheric pressure at lake level to be 92 kPa.

**Solution** The mole fraction of water vapor at the surface of a lake is to be determined and to be compared to the mole fraction of water in the lake.

**Assumptions** 1 Both the air and water vapor are ideal gases. 2 The amount of air dissolved in water is negligible.

**Properties** The saturation pressure of water at  $15^\circ\text{C}$  is 1.7057 kPa (Table A–4).

**Analysis** There exists phase equilibrium at the free surface of the lake, and thus the air at the lake surface is always saturated at the interface temperature.

The air at the water surface is saturated. Therefore, the partial pressure of water vapor in the air at the lake surface will simply be the saturation pressure of water at  $15^\circ\text{C}$ ,

$$P_v = P_{\text{sat}@15^\circ\text{C}} = 1.7057 \text{ kPa}$$

The mole fraction of water vapor in the air at the surface of the lake is determined from Eq. 16–22 to be

$$y_v = \frac{P_v}{P} = \frac{1.7057 \text{ kPa}}{92 \text{ kPa}} = \mathbf{0.0185 \text{ or } 1.85 \text{ percent}}$$

Water contains some dissolved air, but the amount is negligible. Therefore, we can assume the entire lake to be liquid water. Then its mole fraction becomes

$$y_{\text{water,liquid side}} \cong \mathbf{1.0 \text{ or } 100 \text{ percent}}$$

**Discussion** Note that the concentration of water on a molar basis is 100 percent just beneath the air–water interface and less than 2 percent just above it even though the air is assumed to be saturated (so this is the highest value at  $15^\circ\text{C}$ ). Therefore, large discontinuities can occur in the concentrations of a species across phase boundaries.

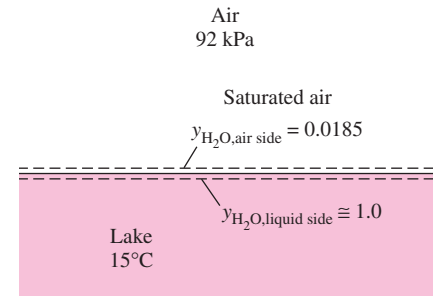


FIGURE 16–24

Schematic for Example 16–8.

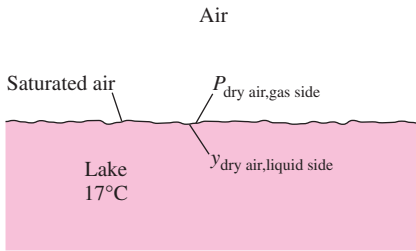


FIGURE 16-25

Schematic for Example 16-9.

**EXAMPLE 16-9** The Amount of Dissolved Air in Water

Determine the mole fraction of air at the surface of a lake whose temperature is 17°C (Fig. 16-25). Take the atmospheric pressure at lake level to be 92 kPa.

**Solution** The mole fraction of air in lake water is to be determined.

**Assumptions** Both the air and vapor are ideal gases.

**Properties** The saturation pressure of water at 17°C is 1.96 kPa (Table A-4). The Henry's constant for air dissolved in water at 290 K is  $H = 62,000$  bar (Table 16-2).

**Analysis** This example is similar to the previous example. Again the air at the water surface is saturated, and thus the partial pressure of water vapor in the air at the lake surface is the saturation pressure of water at 17°C,

$$P_v = P_{\text{sat @ } 17^\circ\text{C}} = 1.96 \text{ kPa}$$

The partial pressure of dry air is

$$P_{\text{dry air}} = P - P_v = 92 - 1.96 = 90.04 \text{ kPa} = 0.9004 \text{ bar}$$

Note that we could have ignored the vapor pressure since the amount of vapor in air is so small with little loss in accuracy (an error of about 2 percent). The mole fraction of air in the water is, from Henry's law,

$$y_{\text{dry air,liquid side}} = \frac{P_{\text{dry air,gas side}}}{H} = \frac{0.9004 \text{ bar}}{62,000 \text{ bar}} = 1.45 \times 10^{-5}$$

**Discussion** This value is very small, as expected. Therefore, the concentration of air in water just below the air–water interface is 1.45 moles per 100,000 moles. But obviously this is enough oxygen for fish and other creatures in the lake. Note that the amount of air dissolved in water will decrease with increasing depth unless phase equilibrium exists throughout the entire lake.

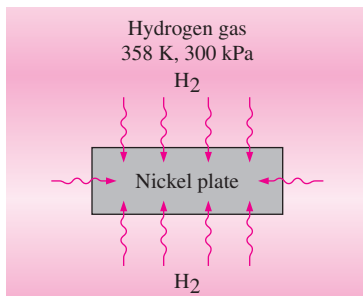


FIGURE 16-26

Schematic for Example 16-10.

**EXAMPLE 16-10** Diffusion of Hydrogen Gas into a Nickel Plate

Consider a nickel plate that is placed into a tank filled with hydrogen gas at 358 K and 300 kPa. Determine the molar and mass density of hydrogen in the nickel plate when phase equilibrium is established (Fig. 16-26).

**Solution** A nickel plate is exposed to hydrogen gas. The density of hydrogen in the plate is to be determined.

**Properties** The molar mass of hydrogen  $\text{H}_2$  is  $M = 2$  kg/kmol, and the solubility of hydrogen in nickel at the specified temperature is given in Table 16-3 to be  $0.00901 \text{ kmol/m}^3 \cdot \text{bar}$ .

**Analysis** Noting that  $300 \text{ kPa} = 3 \text{ bar}$ , the molar density of hydrogen in the nickel plate is determined from Eq. 16-24 to be

$$\begin{aligned} \bar{\rho}_{\text{H}_2,\text{solid side}} &= \mathcal{S} \times P_{\text{H}_2,\text{gas side}} \\ &= (0.00901 \text{ kmol/m}^3 \cdot \text{bar})(3 \text{ bar}) = \mathbf{0.027 \text{ kmol/m}^3} \end{aligned}$$

It corresponds to a mass density of

$$\begin{aligned} \rho_{\text{H}_2,\text{solid side}} &= \bar{\rho}_{\text{H}_2,\text{solid side}} M_{\text{H}_2} \\ &= (0.027 \text{ kmol/m}^3)(2 \text{ kg/kmol}) = \mathbf{0.054 \text{ kg/m}^3} \end{aligned}$$

That is, there will be 0.027 kmol (or 0.054 kg) of  $\text{H}_2$  gas in each  $\text{m}^3$  volume of nickel plate when phase equilibrium is established.

**EXAMPLE 16–11** Composition of Different Phases of a Mixture

In absorption refrigeration systems, a two-phase equilibrium mixture of liquid ammonia ( $\text{NH}_3$ ) and water ( $\text{H}_2\text{O}$ ) is frequently used. Consider one such mixture at  $40^\circ\text{C}$ , shown in Fig. 16–27. If the composition of the liquid phase is 70 percent  $\text{NH}_3$  and 30 percent  $\text{H}_2\text{O}$  by mole numbers, determine the composition of the vapor phase of this mixture.

**Solution** A two-phase mixture of ammonia and water at a specified temperature is considered. The composition of the liquid phase is given, and the composition of the vapor phase is to be determined.

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

**Properties** The saturation pressures of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  at  $40^\circ\text{C}$  are  $P_{\text{H}_2\text{O},\text{sat}} = 7.3851 \text{ kPa}$  and  $P_{\text{NH}_3,\text{sat}} = 1554.33 \text{ kPa}$ .

**Analysis** The vapor pressures are determined from

$$P_{\text{H}_2\text{O},\text{gas side}} = y_{\text{H}_2\text{O},\text{liquid side}} P_{\text{H}_2\text{O},\text{sat}}(T) = 0.30(7.3851 \text{ kPa}) = 2.22 \text{ kPa}$$

$$P_{\text{NH}_3,\text{gas side}} = y_{\text{NH}_3,\text{liquid side}} P_{\text{NH}_3,\text{sat}}(T) = 0.70(1554.33 \text{ kPa}) = 1088.03 \text{ kPa}$$

The total pressure of the mixture is

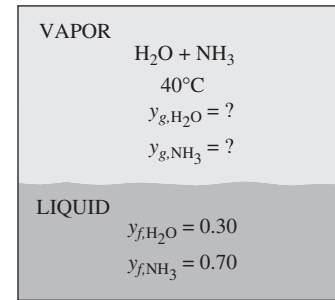
$$P_{\text{total}} = P_{\text{H}_2\text{O}} + P_{\text{NH}_3} = 2.22 + 1088.03 = 1090.25 \text{ kPa}$$

Then the mole fractions in the gas phase are

$$y_{\text{H}_2\text{O},\text{gas side}} = \frac{P_{\text{H}_2\text{O},\text{gas side}}}{P_{\text{total}}} = \frac{2.22 \text{ kPa}}{1090.25 \text{ kPa}} = \mathbf{0.0020}$$

$$y_{\text{NH}_3,\text{gas side}} = \frac{P_{\text{NH}_3,\text{gas side}}}{P_{\text{total}}} = \frac{1088.03 \text{ kPa}}{1090.25 \text{ kPa}} = \mathbf{0.9980}$$

**Discussion** Note that the gas phase consists almost entirely of ammonia, making this mixture very suitable for absorption refrigeration.



**FIGURE 16–27** Schematic for Example 16–11.

**SUMMARY**

An isolated system is said to be in *chemical equilibrium* if no changes occur in the chemical composition of the system. The criterion for chemical equilibrium is based on the second law of thermodynamics, and for a system at a specified temperature and pressure it can be expressed as

$$(dG)_{T,P} = 0$$

For the reaction



where the  $\nu$ 's are the stoichiometric coefficients, the *equilibrium criterion* can be expressed in terms of the Gibbs functions as

$$\nu_C \bar{g}_C + \nu_D \bar{g}_D - \nu_A \bar{g}_A - \nu_B \bar{g}_B = 0$$

which is valid for any chemical reaction regardless of the phases involved.

For reacting systems that consist of ideal gases only, the equilibrium constant  $K_P$  can be expressed as

$$K_P = e^{-\Delta G^*(T)/R_u T}$$

where the *standard-state Gibbs function change*  $\Delta G^*(T)$  and the equilibrium constant  $K_P$  are defined as

$$\Delta G^*(T) = \nu_C \bar{g}_C^*(T) + \nu_D \bar{g}_D^*(T) - \nu_A \bar{g}_A^*(T) - \nu_B \bar{g}_B^*(T)$$

and

$$K_P = \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}}$$

Here,  $P_i$ 's are the partial pressures of the components in atm. The  $K_P$  of ideal-gas mixtures can also be expressed in terms of the mole numbers of the components as

$$K_P = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left( \frac{P}{N_{\text{total}}} \right)^{\Delta \nu}$$

where  $\Delta\nu = \nu_C + \nu_D - \nu_A - \nu_B$ ,  $P$  is the total pressure in atm, and  $N_{\text{total}}$  is the total number of moles present in the reaction chamber, including any inert gases. The equation above is written for a reaction involving two reactants and two products, but it can be extended to reactions involving any number of reactants and products.

The equilibrium constant  $K_p$  of ideal-gas mixtures depends on temperature only. It is independent of the pressure of the equilibrium mixture, and it is not affected by the presence of inert gases. The larger the  $K_p$ , the more complete the reaction. Very small values of  $K_p$  indicate that a reaction does not proceed to any appreciable degree. A reaction with  $K_p > 1000$  is usually assumed to proceed to completion, and a reaction with  $K_p < 0.001$  is assumed not to occur at all. The mixture pressure affects the equilibrium composition, although it does not affect the equilibrium constant  $K_p$ .

The variation of  $K_p$  with temperature is expressed in terms of other thermochemical properties through the *van't Hoff equation*

$$\frac{d(\ln K_p)}{dT} = \frac{\bar{h}_R(T)}{R_u T^2}$$

where  $\bar{h}_R(T)$  is the enthalpy of reaction at temperature  $T$ . For small temperature intervals, it can be integrated to yield

$$\ln \frac{K_{p_2}}{K_{p_1}} \cong \frac{\bar{h}_R}{R_u} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

This equation shows that combustion processes are less complete at higher temperatures since  $K_p$  decreases with temperature for exothermic reactions.

Two phases are said to be in *phase equilibrium* when there is no transformation from one phase to the other. Two phases

of a pure substance are in equilibrium when each phase has the same value of specific Gibbs function. That is,

$$g_f = g_g$$

In general, the number of independent variables associated with a multicomponent, multiphase system is given by the *Gibbs phase rule*, expressed as

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

where IV = the number of independent variables,  $C$  = the number of components, and PH = the number of phases present in equilibrium.

A multicomponent, multiphase system at a specified temperature and pressure is in phase equilibrium when the specific Gibbs function of each component is the same in all phases.

For a gas  $i$  that is weakly soluble in a liquid (such as air in water), the mole fraction of the gas in the liquid  $y_{i,\text{liquid side}}$  is related to the partial pressure of the gas  $P_{i,\text{gas side}}$  by Henry's law

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

where  $H$  is Henry's constant. When a gas is highly soluble in a liquid (such as ammonia in water), the mole fractions of the species of a two-phase mixture in the liquid and gas phases are given approximately by Raoult's law, expressed as

$$P_{i,\text{gas side}} = y_{i,\text{gas side}} P_{\text{total}} = y_{i,\text{liquid side}} P_{i,\text{sat}}(T)$$

where  $P_{\text{total}}$  is the total pressure of the mixture,  $P_{i,\text{sat}}(T)$  is the saturation pressure of species  $i$  at the mixture temperature, and  $y_{i,\text{liquid side}}$  and  $y_{i,\text{gas side}}$  are the mole fractions of species  $i$  in the liquid and vapor phases, respectively.

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## PROBLEMS\*

 **$K_p$  and the Equilibrium Composition of Ideal Gases**

**16-1C** Why is the criterion for chemical equilibrium expressed in terms of the Gibbs function instead of entropy?

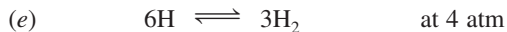
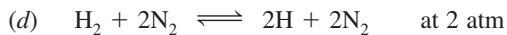
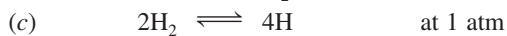
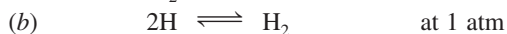
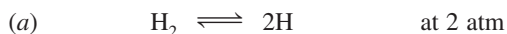
**16-2C** Is a wooden table in chemical equilibrium with the air?

**16-3C** Write three different  $K_p$  relations for reacting ideal-gas mixtures, and state when each relation should be used.

**16-4C** The equilibrium constant of the reaction  $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$  at 1000 K and 1 atm is  $K_{p_1}$ . Express the equilibrium constant of the following reactions at 1000 K in terms of  $K_{p_1}$ :



**16-5C** The equilibrium constant of the dissociation reaction  $\text{H}_2 \rightarrow 2\text{H}$  at 3000 K and 1 atm is  $K_{p_1}$ . Express the equilibrium constants of the following reactions at 3000 K in terms of  $K_{p_1}$ :



**16-6C** Consider a mixture of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$  in equilibrium at a specified temperature and pressure. Now the pressure is doubled.

- (a) Will the equilibrium constant  $K_p$  change?  
 (b) Will the number of moles of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$  change? How?

**16-7C** Consider a mixture of  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{N}_2$  in equilibrium at a specified temperature and pressure. Now the pressure is tripled.

- (a) Will the equilibrium constant  $K_p$  change?  
 (b) Will the number of moles of  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{N}_2$  change? How?

**16-8C** A reaction chamber contains a mixture of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$  in equilibrium at a specified temperature and pres-

sure. How will (a) increasing the temperature at constant pressure and (b) increasing the pressure at constant temperature affect the number of moles of  $\text{CO}_2$ ?

**16-9C** A reaction chamber contains a mixture of  $\text{N}_2$  and  $\text{N}$  in equilibrium at a specified temperature and pressure. How will (a) increasing the temperature at constant pressure and (b) increasing the pressure at constant temperature affect the number of moles of  $\text{N}_2$ ?


**16-10C** A reaction chamber contains a mixture of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$  in equilibrium at a specified temperature and pressure. Now some  $\text{N}_2$  is added to the mixture while the mixture temperature and pressure are kept constant. Will this affect the number of moles of  $\text{O}_2$ ? How?

**16-11C** Which element is more likely to dissociate into its monatomic form at 3000 K,  $\text{H}_2$  or  $\text{N}_2$ ? Why?

**16-12** Using the Gibbs function data, determine the equilibrium constant  $K_p$  for the reaction  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$  at (a) 298 K and (b) 2000 K. Compare your results with the  $K_p$  values listed in Table A-28.

**16-13E** Using Gibbs function data, determine the equilibrium constant  $K_p$  for the reaction  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$  at (a) 537 R and (b) 3240 R. Compare your results with the  $K_p$  values listed in Table A-28. *Answers: (a)  $1.12 \times 10^{40}$ , (b)  $1.90 \times 10^4$*

**16-14** Determine the equilibrium constant  $K_p$  for the process  $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$  at (a) 298 K and (b) 2000 K. Compare your results with the values for  $K_p$  listed in Table A-28.

**16-15**  Study the effect of varying the percent excess air during the steady-flow combustion of hydrogen at a pressure of 1 atm. At what temperature will 97 percent of  $\text{H}_2$  burn into  $\text{H}_2\text{O}$ ? Assume the equilibrium mixture consists of  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$ .



**16-16** Determine the equilibrium constant  $K_p$  for the reaction  $\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O}$  at 25°C. *Answer:  $1.96 \times 10^{140}$*


**16-17** Using the Gibbs function data, determine the equilibrium constant  $K_p$  for the dissociation process  $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$  at (a) 298 K and (b) 1800 K. Compare your results with the  $K_p$  values listed in Table A-28.


**16-18** Using the Gibbs function data, determine the equilibrium constant  $K_p$  for the reaction  $\text{H}_2\text{O} \rightleftharpoons \frac{1}{2}\text{H}_2 + \text{OH}$  at 25°C. Compare your result with the  $K_p$  value listed in Table A-28.

**16-19** Determine the temperature at which 5 percent of diatomic oxygen ( $\text{O}_2$ ) dissociates into monatomic oxygen ( $\text{O}$ ) at a pressure of 3 atm. *Answer: 3133 K*

**16-20** Repeat Prob. 16-19 for a pressure of 6 atm.

\*Problems designated by a "C" are concept questions, and students are encouraged to answer them all. Problems designated by an "E" are in English units, and the SI users can ignore them. Problems with a CD-EES icon  are solved using EES, and complete solutions together with parametric studies are included on the enclosed DVD. Problems with a computer-EES icon  are comprehensive in nature, and are intended to be solved with a computer, preferably using the EES software that accompanies this text.

**16-21**  Carbon monoxide is burned with 100 percent excess air during a steady-flow process at a pressure of 1 atm. At what temperature will 97 percent of CO burn to CO<sub>2</sub>? Assume the equilibrium mixture consists of CO<sub>2</sub>, CO, O<sub>2</sub>, and N<sub>2</sub>. *Answer: 2276 K*

**16-22**  Reconsider Prob. 16-21. Using EES (or other) software, study 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 burns into CO<sub>2</sub>. Plot the temperature against the percent excess air, and discuss the results.

**16-23E** Repeat Prob. 16-21 using data in English units.

**16-24** Hydrogen is burned with 150 percent theoretical air during a steady-flow process at a pressure of 1 atm. At what temperature will 98 percent of H<sub>2</sub> burn to H<sub>2</sub>O? Assume the equilibrium mixture consists of H<sub>2</sub>O, H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>.

**16-25** Air (79 percent N<sub>2</sub> and 21 percent O<sub>2</sub>) is heated to 2000 K at a constant pressure of 2 atm. Assuming the equilibrium mixture consists of N<sub>2</sub>, O<sub>2</sub>, and NO, determine the equilibrium composition at this state. Is it realistic to assume that no monatomic oxygen or nitrogen will be present in the equilibrium mixture? Will the equilibrium composition change if the pressure is doubled at constant temperature?

**16-26** Hydrogen (H<sub>2</sub>) is heated to 3200 K at a constant pressure of 8 atm. Determine the percentage of H<sub>2</sub> that will dissociate into H during this process. *Answer: 5.0 percent*

**16-27** Carbon dioxide (CO<sub>2</sub>) is heated to 2400 K at a constant pressure of 3 atm. Determine the percentage of CO<sub>2</sub> that will dissociate into CO and O<sub>2</sub> during this process.

**16-28** A mixture of 1 mol of CO and 3 mol of O<sub>2</sub> is heated to 2200 K at a pressure of 2 atm. Determine the equilibrium composition, assuming the mixture consists of CO<sub>2</sub>, CO, and O<sub>2</sub>. *Answers: 0.995CO<sub>2</sub>, 0.005CO, 2.5025O<sub>2</sub>*

**16-29E** A mixture of 2 mol of CO, 2 mol of O<sub>2</sub>, and 6 mol of N<sub>2</sub> is heated to 4320 R at a pressure of 3 atm. Determine the equilibrium composition of the mixture.

*Answers: 1.93CO<sub>2</sub>, 0.07CO, 1.035O<sub>2</sub>, 6N<sub>2</sub>*

**16-30** A mixture of 3 mol of N<sub>2</sub>, 1 mol of O<sub>2</sub>, and 0.1 mol of Ar is heated to 2400 K at a constant pressure of 10 atm. Assuming the equilibrium mixture consists of N<sub>2</sub>, O<sub>2</sub>, Ar, and NO, determine the equilibrium composition.

*Answers: 0.0823NO, 2.9589N<sub>2</sub>, 0.9589O<sub>2</sub>, 0.1Ar*

**16-31** Determine the mole fraction of sodium that ionizes according to the reaction  $\text{Na} \rightleftharpoons \text{Na}^+ + e^-$  at 2000 K and 0.8 atm ( $K_p = 0.668$  for this reaction). *Answer: 67.5 percent*

**16-32** Liquid propane (C<sub>3</sub>H<sub>8</sub>) enters a combustion chamber at 25°C at a rate of 1.2 kg/min where it is mixed and burned with 150 percent excess air that enters the combustion chamber at 12°C. If the combustion gases consist of CO<sub>2</sub>, H<sub>2</sub>O, CO, O<sub>2</sub>, and N<sub>2</sub> that exit at 1200 K and 2 atm, determine

(a) the equilibrium composition of the product gases and (b) the rate of heat transfer from the combustion chamber. Is it realistic to disregard the presence of NO in the product gases?

*Answers: (a) 3CO<sub>2</sub>, 7.5O<sub>2</sub>, 4H<sub>2</sub>O, 47N<sub>2</sub>, (b) 5066 kJ/min*

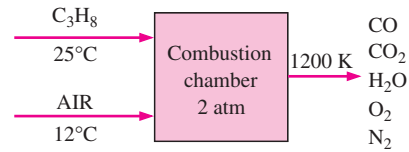



FIGURE P16-32

**16-33**  Reconsider Prob. 16-32. Using EES (or other) software, investigate if it is realistic to disregard the presence of NO in the product gases?

**16-34E** A steady-flow combustion chamber is supplied with CO gas at 560 R and 16 psia at a rate of 12.5 ft<sup>3</sup>/min and with oxygen (O<sub>2</sub>) at 537 R and 16 psia at a rate of 0.7 lbm/min. The combustion products leave the combustion chamber at 3600 R and 16 psia. If the combustion gases consist of CO<sub>2</sub>, CO, and O<sub>2</sub>, determine (a) the equilibrium composition of the product gases and (b) the rate of heat transfer from the combustion chamber.

**16-35** Oxygen (O<sub>2</sub>) is heated during a steady-flow process at 1 atm from 298 to 3000 K at a rate of 0.5 kg/min. Determine the rate of heat supply needed during this process, assuming (a) some O<sub>2</sub> dissociates into O and (b) no dissociation takes place.

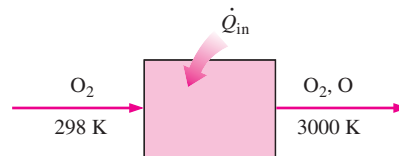
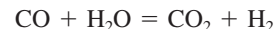


FIGURE P16-35

**16-36** Estimate  $K_p$  for the following equilibrium reaction at 2500 K:



At 2000 K it is known that the enthalpy of reaction is  $-26176$  kJ/kmol and  $K_p$  is 0.2209. Compare your result with the value obtained from the definition of the equilibrium constant.

**16-37** A constant-volume tank contains a mixture of 1 kmol H<sub>2</sub> and 1 kmol O<sub>2</sub> at 25°C and 1 atm. The contents are ignited. Determine the final temperature and pressure in the tank when the combustion gases are H<sub>2</sub>O, H<sub>2</sub>, and O<sub>2</sub>.

## Simultaneous Reactions

**16-38C** What is the equilibrium criterion for systems that involve two or more simultaneous chemical reactions?

**16-39C** When determining the equilibrium composition of a mixture involving simultaneous reactions, how would you determine the number of  $K_p$  relations needed?

**16-40** One mole of  $\text{H}_2\text{O}$  is heated to 3400 K at a pressure of 1 atm. Determine the equilibrium composition, assuming that only  $\text{H}_2\text{O}$ ,  $\text{OH}$ ,  $\text{O}_2$ , and  $\text{H}_2$  are present. *Answers:*  $0.574\text{H}_2\text{O}$ ,  $0.308\text{H}_2$ ,  $0.095\text{O}_2$ ,  $0.236\text{OH}$

**16-41** A mixture of 2 mol of  $\text{CO}_2$  and 1 mol of  $\text{O}_2$  is heated to 3200 K at a pressure of 2 atm. Determine the equilibrium composition of the mixture, assuming that only  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{O}_2$ , and  $\text{O}$  are present.

**16-42** Air (21 percent  $\text{O}_2$ , 79 percent  $\text{N}_2$ ) is heated to 3000 K at a pressure of 2 atm. Determine the equilibrium composition, assuming that only  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{O}$ , and  $\text{NO}$  are present. Is it realistic to assume that no  $\text{N}$  will be present in the final equilibrium mixture?

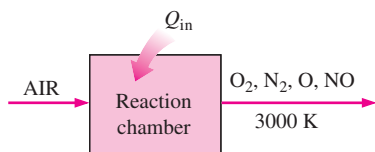






FIGURE P16-42

**16-43E**  Air (21 percent  $\text{O}_2$ , 79 percent  $\text{N}_2$ ) is heated to 5400 R at a pressure of 1 atm. Determine the equilibrium composition, assuming that only  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{O}$ , and  $\text{NO}$  are present. Is it realistic to assume that no  $\text{N}$  will be present in the final equilibrium mixture?

**16-44E**  Reconsider Prob. 16-43E. Use EES (or other) software to obtain the equilibrium solution. Compare your solution technique with that used in Prob. 16-43E.

**16-45** Water vapor ( $\text{H}_2\text{O}$ ) is heated during a steady-flow process at 1 atm from 298 to 3000 K at a rate of 0.2 kg/min. Determine the rate of heat supply needed during this process, assuming (a) some  $\text{H}_2\text{O}$  dissociates into  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{OH}$  and (b) no dissociation takes place. *Answers:* (a) 2055 kJ/min, (b) 1404 kJ/min

**16-46**  Reconsider Prob. 16-45. Using EES (or other) software, study the effect of the final temperature on the rate of heat supplied for the two cases. Let the final temperature vary from 2500 to 3500 K. For each of the two cases, plot the rate of heat supplied as a function final temperature.

**16-47**  Ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}(g)$ ) at  $25^\circ\text{C}$  is burned in a steady-flow adiabatic combustion chamber with 40 percent excess air that also enters at  $25^\circ\text{C}$ . Determine the adiabatic flame temperature of the products at 1 atm assuming the significant equilibrium reactions are  $\text{CO}_2 = \text{CO} + \frac{1}{2}\text{O}_2$  and  $\frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2 = \text{NO}$ . Plot the adiabatic flame temperature and kmoles of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{NO}$  at equilibrium for values of percent excess air between 10 and 100 percent.

## Variations of $K_p$ with Temperature

**16-48C** What is the importance of the van't Hoff equation?

**16-49C** Will a fuel burn more completely at 2000 or 2500 K?

**16-50** Estimate the enthalpy of reaction  $\bar{h}_R$  for the combustion process of carbon monoxide at 2200 K, using (a) enthalpy data and (b)  $K_p$  data.

**16-51E** Estimate the enthalpy of reaction  $\bar{h}_R$  for the combustion process of carbon monoxide at 3960 R, using (a) enthalpy data and (b)  $K_p$  data. *Answers:* (a)  $-119,030$  Btu/lbmol, (b)  $-119,041$  Btu/lbmol

**16-52** Using the enthalpy of reaction  $\bar{h}_R$  data and the  $K_p$  value at 2400 K, estimate the  $K_p$  value of the combustion process  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$  at 2600 K. *Answer:* 104.1

**16-53** Estimate the enthalpy of reaction  $\bar{h}_R$  for the dissociation process  $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$  at 2200 K, using (a) enthalpy data and (b)  $K_p$  data.

**16-54** Estimate the enthalpy of reaction  $\bar{h}_R$  for the dissociation process  $\text{O}_2 \rightleftharpoons 2\text{O}$  at 3100 K, using (a) enthalpy data and (b)  $K_p$  data. *Answers:* (a) 513,614 kJ/kmol, (b) 512,808 kJ/kmol

**16-55** Estimate the enthalpy of reaction for the equilibrium reaction  $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$  at 2500 K, using (a) enthalpy data and (b)  $K_p$  data.

## Phase Equilibrium

**16-56C** Consider a tank that contains a saturated liquid-vapor mixture of water in equilibrium. Some vapor is now allowed to escape the tank at constant temperature and pressure. Will this disturb the phase equilibrium and cause some of the liquid to evaporate?

**16-57C** Consider a two-phase mixture of ammonia and water in equilibrium. Can this mixture exist in two phases at the same temperature but at a different pressure?

**16-58C** Using the solubility data of a solid in a specified liquid, explain how you would determine the mole fraction of the solid in the liquid at the interface at a specified temperature.

**16-59C** Using solubility data of a gas in a solid, explain how you would determine the molar concentration of the gas in the solid at the solid-gas interface at a specified temperature.

**16-60C** Using the Henry's constant data for a gas dissolved in a liquid, explain how you would determine the mole fraction of the gas dissolved in the liquid at the interface at a specified temperature.

**16-61** Show that a mixture of saturated liquid water and saturated water vapor at 100°C satisfies the criterion for phase equilibrium.

**16-62** Show that a mixture of saturated liquid water and saturated water vapor at 300 kPa satisfies the criterion for phase equilibrium.

**16-63** Show that a saturated liquid–vapor mixture of refrigerant-134a at  $-10^{\circ}\text{C}$  satisfies the criterion for phase equilibrium.

**16-64** Consider a mixture of oxygen and nitrogen in the gas phase. How many independent properties are needed to fix the state of the system? *Answer: 3*

**16-65** In absorption refrigeration systems, a two-phase equilibrium mixture of liquid ammonia ( $\text{NH}_3$ ) and water ( $\text{H}_2\text{O}$ ) is frequently used. Consider a liquid–vapor mixture of ammonia and water in equilibrium at  $30^{\circ}\text{C}$ . If the composition of the liquid phase is 60 percent  $\text{NH}_3$  and 40 percent  $\text{H}_2\text{O}$  by mole numbers, determine the composition of the vapor phase of this mixture. Saturation pressure of  $\text{NH}_3$  at  $30^{\circ}\text{C}$  is 1167.4 kPa.

**16-66** Consider a liquid–vapor mixture of ammonia and water in equilibrium at  $25^{\circ}\text{C}$ . If the composition of the liquid phase is 50 percent  $\text{NH}_3$  and 50 percent  $\text{H}_2\text{O}$  by mole numbers, determine the composition of the vapor phase of this mixture. Saturation pressure of  $\text{NH}_3$  at  $25^{\circ}\text{C}$  is 1003.5 kPa. *Answers: 0.31 percent, 99.69 percent*

**16-67** A two-phase mixture of ammonia and water is in equilibrium at  $50^{\circ}\text{C}$ . If the composition of the vapor phase is 99 percent  $\text{NH}_3$  and 1 percent  $\text{H}_2\text{O}$  by mole numbers, determine the composition of the liquid phase of this mixture. Saturation pressure of  $\text{NH}_3$  at  $50^{\circ}\text{C}$  is 2033.5 kPa.

**16-68** Using the liquid–vapor equilibrium diagram of an oxygen–nitrogen mixture, determine the composition of each phase at 80 K and 100 kPa.

**16-69** Using the liquid–vapor equilibrium diagram of an oxygen–nitrogen mixture, determine the composition of each phase at 84 K and 100 kPa.

**16-70** Using the liquid–vapor equilibrium diagram of an oxygen–nitrogen mixture at 100 kPa, determine the temperature at which the composition of the vapor phase is 79 percent  $\text{N}_2$  and 21 percent  $\text{O}_2$ . *Answer: 82 K*

**16-71** Using the liquid–vapor equilibrium diagram of an oxygen–nitrogen mixture at 100 kPa, determine the temperature at which the composition of the liquid phase is 30 percent  $\text{N}_2$  and 70 percent  $\text{O}_2$ .

**16-72** Consider a rubber plate that is in contact with nitrogen gas at 298 K and 250 kPa. Determine the molar and mass density of nitrogen in the rubber at the interface.

**16-73** A wall made of natural rubber separates  $\text{O}_2$  and  $\text{N}_2$  gases at  $25^{\circ}\text{C}$  and 500 kPa. Determine the molar concentrations of  $\text{O}_2$  and  $\text{N}_2$  in the wall.

**16-74** Consider a glass of water in a room at  $27^{\circ}\text{C}$  and 97 kPa. If the relative humidity in the room is 100 percent and the water and the air are in thermal and phase equilibrium, determine (a) the mole fraction of the water vapor in the air and (b) the mole fraction of air in the water.

**16-75E** Water is sprayed into air at  $80^{\circ}\text{F}$  and 14.3 psia, and the falling water droplets are collected in a container on the floor. Determine the mass and mole fractions of air dissolved in the water.

**16-76** Consider a carbonated drink in a bottle at  $27^{\circ}\text{C}$  and 130 kPa. Assuming the gas space above the liquid consists of a saturated mixture of  $\text{CO}_2$  and water vapor and treating the drink as water, determine (a) the mole fraction of the water vapor in the  $\text{CO}_2$  gas and (b) the mass of dissolved  $\text{CO}_2$  in a 300-ml drink.


### Review Problems


**16-77** Using the Gibbs function data, determine the equilibrium constant  $K_p$  for the dissociation process  $\text{O}_2 \rightleftharpoons 2\text{O}$  at 2000 K. Compare your result with the  $K_p$  value listed in Table A-28. *Answer:  $4.4 \times 10^{-7}$*

**16-78** A mixture of 1 mol of  $\text{H}_2$  and 1 mol of Ar is heated at a constant pressure of 1 atm until 15 percent of  $\text{H}_2$  dissociates into monatomic hydrogen (H). Determine the final temperature of the mixture.

**16-79** A mixture of 1 mol of  $\text{H}_2\text{O}$ , 2 mol of  $\text{O}_2$ , and 5 mol of  $\text{N}_2$  is heated to 2200 K at a pressure of 5 atm. Assuming the equilibrium mixture consists of  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{H}_2$ , determine the equilibrium composition at this state. Is it realistic to assume that no OH will be present in the equilibrium mixture?

**16-80** Determine the mole fraction of argon that ionizes according to the reaction  $\text{Ar} \rightleftharpoons \text{Ar}^+ + e^-$  at 10,000 K and 0.35 atm ( $K_p = 0.00042$  for this reaction).


**16-81**  Methane gas ( $\text{CH}_4$ ) at  $25^{\circ}\text{C}$  is burned with the stoichiometric amount of air at  $25^{\circ}\text{C}$  during an adiabatic steady-flow combustion process at 1 atm. Assuming the product gases consist of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{N}_2$ , and  $\text{O}_2$ , determine (a) the equilibrium composition of the product gases and (b) the exit temperature.

**16-82**  Reconsider Prob. 16-81. Using EES (or other) software, study the effect of excess air on the equilibrium composition and the exit temperature by varying the percent excess air from 0 to 200 percent. Plot the exit temperature against the percent excess air, and discuss the results.


**16-83** A constant-volume tank contains a mixture of 1 mol of  $H_2$  and 0.5 mol of  $O_2$  at  $25^\circ C$  and 1 atm. The contents of the tank are ignited, and the final temperature and pressure in the tank are 2800 K and 5 atm, respectively. If the combustion gases consist of  $H_2O$ ,  $H_2$ , and  $O_2$ , determine (a) the equilibrium composition of the product gases and (b) the amount of heat transfer from the combustion chamber. Is it realistic to assume that no OH will be present in the equilibrium mixture?  
*Answers: (a)  $0.944H_2O, 0.056H_2, 0.028O_2$ , (b) 132,574 J/mol  $H_2$*

**16-84** A mixture of 2 mol of  $H_2O$  and 3 mol of  $O_2$  is heated to 3600 K at a pressure of 8 atm. Determine the equilibrium composition of the mixture, assuming that only  $H_2O$ , OH,  $O_2$ , and  $H_2$  are present.

**16-85** A mixture of 3 mol of  $CO_2$  and 3 mol of  $O_2$  is heated to 3400 K at a pressure of 2 atm. Determine the equilibrium composition of the mixture, assuming that only  $CO_2$ , CO,  $O_2$ , and O are present. *Answers:  $1.313CO_2, 1.687CO, 3.187O_2, 1.314O$*

**16-86**  Reconsider Prob. 16-85. Using EES (or other) software, study the effect of pressure on the equilibrium composition by varying pressure from 1 atm to 10 atm. Plot the amount of CO present at equilibrium as a function of pressure.

**16-87** Estimate the enthalpy of reaction  $\bar{h}_R$  for the combustion process of hydrogen at 2400 K, using (a) enthalpy data and (b)  $K_p$  data.  
*Answers: (a)  $-252,377$  kJ/kmol, (b)  $-252,047$  kJ/kmol*

**16-88**  Reconsider Prob. 16-87. Using EES (or other) software, investigate the effect of temperature on the enthalpy of reaction using both methods by varying the temperature from 2000 to 3000 K.

**16-89** Using the enthalpy of reaction  $\bar{h}_R$  data and the  $K_p$  value at 2800 K, estimate the  $K_p$  value of the dissociation process  $O_2 \rightleftharpoons 2O$  at 3000 K.

**16-90** Show that when the three phases of a pure substance are in equilibrium, the specific Gibbs function of each phase is the same.

**16-91** Show 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.


**16-92** A constant-volume tank initially contains 1 kmol of carbon monoxide CO and 3 kmol of oxygen  $O_2$  (no nitrogen) at  $25^\circ C$  and 2 atm. Now the mixture is ignited and the CO burns completely to carbon dioxide  $CO_2$ . If the final temperature in the tank is 500 K, determine the final pressure in the tank and the amount of heat transfer. Is it realistic to assume that there will be no CO in the tank when chemical equilibrium is reached?


**16-93** Using Henry's law, show that the dissolved gases in a liquid can be driven off by heating the liquid.


**16-94** Consider a glass of water in a room at  $25^\circ C$  and 100 kPa. If the relative humidity in the room is 70 percent and the water and the air are in thermal equilibrium, determine (a) the mole fraction of the water vapor in the room air, (b) the mole fraction of the water vapor in the air adjacent to the water surface, and (c) the mole fraction of air in the water near the surface.

**16-95** Repeat Prob. 16-94 for a relative humidity of 25 percent.

**16-96** A carbonated drink is fully charged with  $CO_2$  gas at  $17^\circ C$  and 600 kPa such that the entire bulk of the drink is in thermodynamic equilibrium with the  $CO_2$ -water vapor mixture. Now consider a 2-L soda bottle. If the  $CO_2$  gas in that bottle were to be released and stored in a container at  $20^\circ C$  and 100 kPa, determine the volume of the container.

**16-97**  Ethyl alcohol ( $C_2H_5OH(g)$ ) at  $25^\circ C$  is burned in a steady-flow adiabatic combustion chamber with 40 percent excess air that also enters at  $25^\circ C$ . Determine the adiabatic flame temperature of the products at 1 atm assuming the only significant equilibrium reaction is  $CO_2 = CO + \frac{1}{2}O_2$ . Plot the adiabatic flame temperature as the percent excess air varies from 10 to 100 percent.

**16-98**  Tabulate the natural log of the equilibrium constant as a function of temperature between 298 to 3000 K for the equilibrium reaction  $CO + H_2O = CO_2 + H_2$ . Compare your results to those obtained by combining the  $\ln K_p$  values for the two equilibrium reactions  $CO_2 = CO + \frac{1}{2}O_2$  and  $H_2O = H_2 + \frac{1}{2}O_2$  given in Table A-28.

**16-99**  It is desired to control the amount of CO in the products of combustion of octane  $C_8H_{18}$  so that the volume fraction of CO in the products is less than 0.1 percent. Determine the percent theoretical air required for the combustion of octane at 5 atm such that the reactant and product temperatures are 298 K and 2000 K, respectively. Determine the heat transfer per kmol of octane for this process if the combustion occurs in a steady-flow combustion chamber. Plot the percent theoretical air required for 0.1 percent CO in the products as a function of product pressures between 100 and 2300 kPa.

### Fundamentals of Engineering (FE) Exam Problems

**16-100** If the equilibrium constant for the reaction  $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$  is  $K$ , the equilibrium constant for the reaction  $2H_2O \rightarrow 2H_2 + O_2$  at the same temperature is  
 (a)  $1/K$  (b)  $1/(2K)$  (c)  $2K$  (d)  $K^2$  (e)  $1/K^2$

**16-101** If the equilibrium constant for the reaction  $CO + \frac{1}{2}O_2 \rightarrow CO_2$  is  $K$ , the equilibrium constant for the reaction  $CO_2 + 3N_2 \rightarrow CO + \frac{1}{2}O_2 + 3N_2$  at the same temperature is  
 (a)  $1/K$  (b)  $1/(K + 3)$  (c)  $4K$  (d)  $K$  (e)  $1/K^2$

**16-102** The equilibrium constant for the reaction  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$  at 1 atm and  $1500^\circ\text{C}$  is given to be  $K$ . Of the reactions given below, all at  $1500^\circ\text{C}$ , the reaction that has a different equilibrium constant is

- (a)  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$  at 5 atm  
 (b)  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$  at 1 atm  
 (c)  $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$  at 2 atm  
 (d)  $\text{H}_2 + \frac{1}{2}\text{O}_2 + 3\text{N}_2 \rightarrow \text{H}_2\text{O} + 3\text{N}_2$  at 5 atm  
 (e)  $\text{H}_2 + \frac{1}{2}\text{O}_2 + 3\text{N}_2 \rightarrow \text{H}_2\text{O} + 3\text{N}_2$  at 1 atm

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

- (a)  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$   
 (b)  $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$   
 (c)  $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$   
 (d)  $\text{N}_2 \rightarrow 2\text{N}$   
 (e) all of the above.

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

- (a)  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$   
 (b)  $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$   
 (c)  $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$   
 (d)  $\text{N}_2 \rightarrow 2\text{N}$   
 (e) all of the above.

**16-105** Moist air is heated to a very high temperature. If the equilibrium composition consists of  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{OH}$ ,  $\text{H}_2$ , and  $\text{NO}$ , the number of equilibrium constant relations needed to determine the equilibrium composition of the mixture is

- (a) 1 (b) 2 (c) 3 (d) 4 (e) 5

**16-106** Propane  $\text{C}_3\text{H}_8$  is burned with air, and the combustion products consist of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{OH}$ ,  $\text{H}_2$ , and  $\text{NO}$ . The number of equilibrium constant relations needed to determine the equilibrium composition of the mixture is

- (a) 1 (b) 2 (c) 3 (d) 4 (e) 5

**16-107** Consider a gas mixture that consists of three components. The number of independent variables that need to be specified to fix the state of the mixture is

- (a) 1 (b) 2 (c) 3 (d) 4 (e) 5

**16-108** The value of Henry's constant for  $\text{CO}_2$  gas dissolved in water at 290 K is 12.8 MPa. Consider water exposed to atmospheric air at 100 kPa that contains 3 percent  $\text{CO}_2$  by volume. Under phase equilibrium conditions, the mole fraction of  $\text{CO}_2$  gas dissolved in water at 290 K is

- (a)  $2.3 \times 10^{-4}$  (b)  $3.0 \times 10^{-4}$  (c)  $0.80 \times 10^{-4}$   
 (d)  $2.2 \times 10^{-4}$  (e)  $5.6 \times 10^{-4}$

**16-109** The solubility of nitrogen gas in rubber at  $25^\circ\text{C}$  is  $0.00156 \text{ kmol/m}^3 \cdot \text{bar}$ . When phase equilibrium is established, the density of nitrogen in a rubber piece placed in a nitrogen gas chamber at 800 kPa is

- (a)  $0.012 \text{ kg/m}^3$  (b)  $0.35 \text{ kg/m}^3$  (c)  $0.42 \text{ kg/m}^3$   
 (d)  $0.56 \text{ kg/m}^3$  (e)  $0.078 \text{ kg/m}^3$

### Design and Essay Problems

**16-110** An article that appeared in the *Reno Gazette-Journal* on May 18, 1992, quotes an inventor as saying that he has turned water into motor vehicle fuel in a breakthrough that would increase engine efficiency, save gasoline, and reduce smog. There is also a picture of a car that the inventor has modified to run on half water and half gasoline. The inventor claims that sparks from catalytic poles in the converted engine break down the water into oxygen and hydrogen, which is burned with the gasoline. He adds that hydrogen has a higher energy density than carbon and the high-energy density enables one to get more power. The inventor states that the fuel efficiency of his car increased from 20 mpg (miles per gallon) to more than 50 mpg of gasoline as a result of conversion and notes that the conversion has sharply reduced emissions of hydrocarbons, carbon monoxide, and other exhaust pollutants.

Evaluate the claims made by the inventor, and write a report that is to be submitted to a group of investors who are considering financing this invention.

**16-111** Automobiles are major emitters of air pollutants such as  $\text{NO}_x$ ,  $\text{CO}$ , and hydrocarbons HC. Find out the legal limits of these pollutants in your area, and estimate the total amount of each pollutant, in kg, that would be produced in your town if all the cars were emitting pollutants at the legal limit. State your assumptions.