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# Thermodynamics II

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# Objectives

- 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.

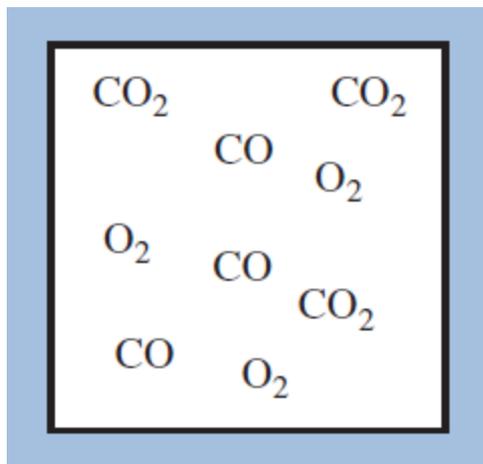
# CRITERION FOR CHEMICAL EQUILIBRIUM

We may know the temperature, pressure, and composition (thus the state) of a system but we are unable to predict whether the system is in chemical equilibrium.

The increase of entropy principle

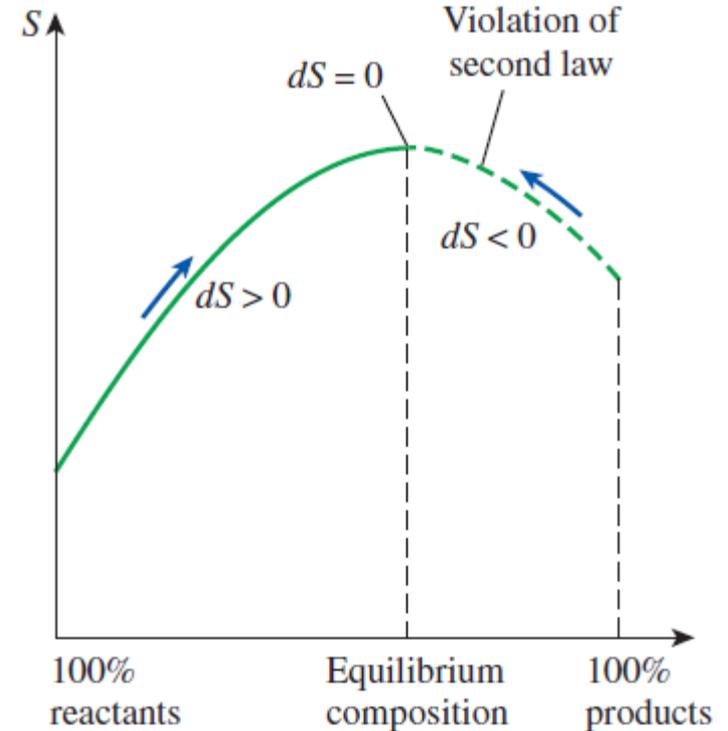
$$dS_{\text{sys}} \geq \frac{\delta Q}{T}$$

A chemical reaction in an adiabatic chamber proceeds in the direction of increasing entropy. When the entropy reaches a maximum, the reaction stops.



**FIGURE 16-1**

A reaction chamber that contains a mixture of CO<sub>2</sub>, CO, and O<sub>2</sub> at a specified temperature and pressure.



**FIGURE 16-2**

Equilibrium criteria for a chemical reaction that takes place adiabatically.

Combining the first- and the second-law relations for the control mass in the figure

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

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

$$(dG)_{T,P} = dH - T dS - S dT$$

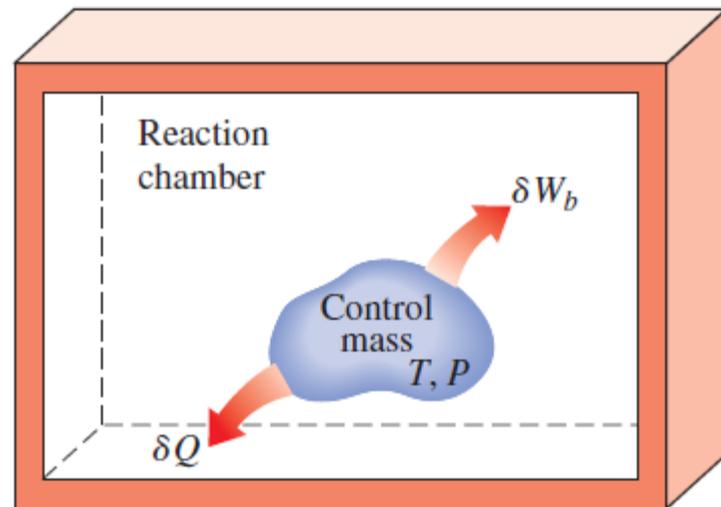
$$= (dU + P dV + V dP) - T dS - S dT$$

$$= dU + P dV - T dS$$

from the two equations  $(dG)_{T,P} \leq 0$

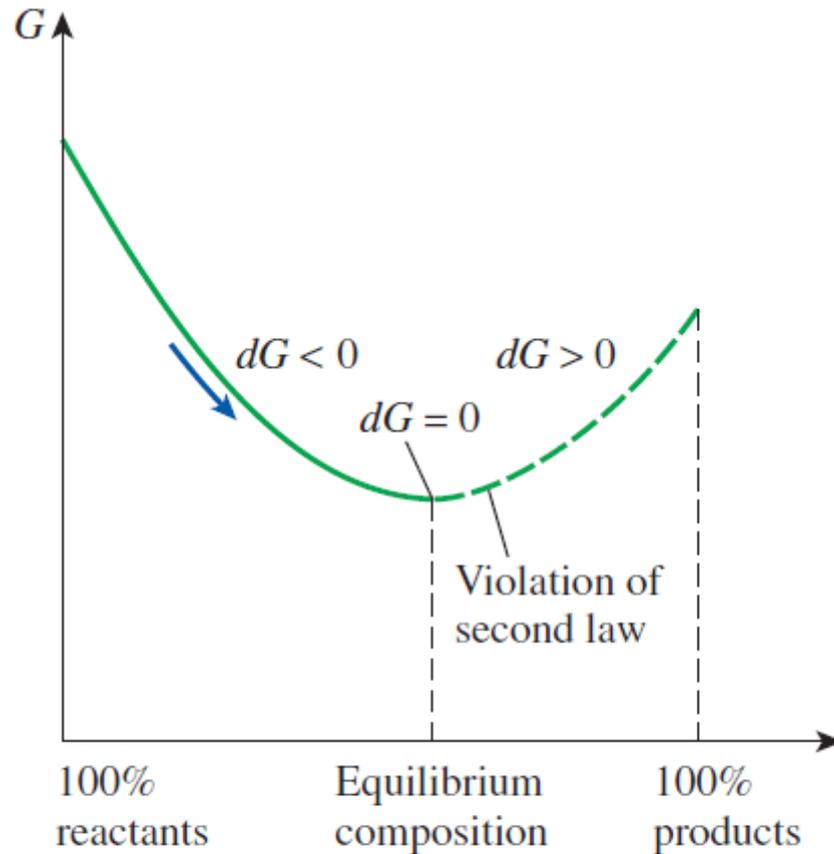
A chemical reaction at a specified  $T$  and  $P$  proceeds in the direction of a decreasing Gibbs function. The reaction stops and chemical equilibrium is established when the Gibbs function attains a minimum value. Therefore, the criterion for chemical equilibrium is

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



**FIGURE 16-3**

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



**FIGURE 16-4**

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

To obtain a relation for chemical equilibrium in terms of the properties of the individual components, we consider a mixture of four chemical components  $A$ ,  $B$ ,  $C$ , and  $D$  that exist in equilibrium at a specified  $T$  and  $P$ .



From the equilibrium criterion

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

$$\bar{g}_C dN_C + \bar{g}_D dN_D + \bar{g}_A dN_A + \bar{g}_B dN_B = 0$$

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



the  $\nu$ 's are the stoichiometric coefficients

$$dN_A = -\varepsilon \nu_A \quad dN_C = \varepsilon \nu_C$$

$$dN_B = -\varepsilon \nu_B \quad dN_D = \varepsilon \nu_D$$

$\varepsilon$  is the proportionality constant. Substituting,

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

**Criterion for chemical equilibrium**

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

Reaction chamber  
 $T, P$

$N_A$  moles of  $A$

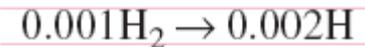
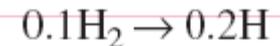
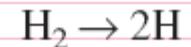
$N_B$  moles of  $B$

$N_C$  moles of  $C$

$N_D$  moles of  $D$



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.



$$\nu_{H_2} = 1$$

$$\nu_H = 2$$

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

$$(\Delta\bar{g})_T = \Delta\bar{h} \xrightarrow{0} T(\Delta\bar{s})_T = -T(\Delta\bar{s})_T = R_u T \ln \frac{P_2}{P_1}$$

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

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

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

(16-9)

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

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

## THE EQUILIBRIUM CONSTANT FOR IDEAL- GAS MIXTURES

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

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

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

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

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.

$$P_i = y_i P = \frac{N_i}{N_{\text{total}}} P \quad \text{Partial pressure in terms of mole numbers}$$

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

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

(1) In terms of partial pressures

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

(2) In terms of  $\Delta G^*(T)$

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

(3) In terms of the equilibrium composition

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

**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.

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

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

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

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

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.

## EXAMPLE 16–2 Producing Hydrogen by Heating Water Vapor to High Temperature

As an alternative to electrolysis, hydrogen gas can be produced thermally in accordance with the dissociation process  $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$  by heating water vapor to very high temperatures (Fig. 16–8). Determine the percentage of water vapor that can be separated into hydrogen and oxygen when this reaction occurs at 4000 K and 10 kPa.

*Stoichiometric:*  $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$  (thus  $\nu_{\text{H}_2\text{O}} = 1$ ,  $\nu_{\text{H}_2} = 1$ , and  $\nu_{\text{O}_2} = 0.5$ )

*Actual:*

$$\text{H}_2\text{O} \longrightarrow \underbrace{x\text{H}_2\text{O}}_{\substack{\text{reactants} \\ \text{(leftover)}}} + \underbrace{y\text{H}_2 + z\text{O}_2}_{\text{products}}$$

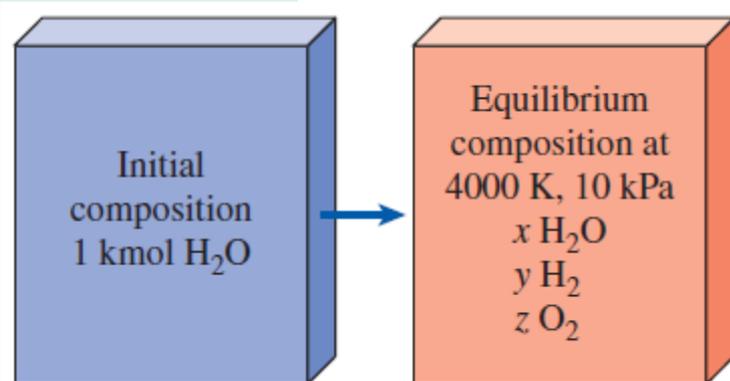
*H balance:*  $2 = 2x + 2y \longrightarrow y = 1 - x$

*O balance:*  $1 = x + 2z \longrightarrow z = (1 - x)/2$

*Total number of moles:*  $N_{\text{total}} = x + y + z = 1.5 - 0.5x$

*Pressure (in atm):*  $P = 10 \text{ kPa} = 0.09869 \text{ atm}$  (since  $1 \text{ atm} = 101.325 \text{ kPa}$ )

The equilibrium constant for the reaction  $\text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$  at 4000 K is given in Table A-28 to be  $\ln K_p = -0.542$  and thus  $K_p = 0.5816$ .



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

$$0.5816 = \frac{(1 - x)[(1 - x)/2]^{1/2}}{x} \left( \frac{0.09869}{1.5 - 0.5x} \right)^{1 + 0.5 - 1}$$

$$x = 0.222$$

Fraction of dissociation =  $1 - x = 1 - 0.222 = \mathbf{0.778}$  or **77.8 percent**

# SOME REMARKS ABOUT THE $K_p$ 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. 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 example, from Table A–28,

$$K_p = 0.1147 \times 10^{11} \quad \text{for} \quad \text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O} \quad \text{at 1000 K}$$

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

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

**3. The larger the  $K_p$ , the more complete the reaction.** If the equilibrium composition consists largely of product gases, the partial pressures of the products are considerably larger than the partial pressures of the reactants, 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. Reactions with very small  $K_p$  values at a specified temperature can be neglected.

**4. The mixture pressure affects the equilibrium composition** (although it does not affect the equilibrium constant  $K_p$ ). 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.

$\text{H}_2 \rightarrow 2\text{H}$		
$P = 1 \text{ atm}$		
$T, \text{ K}$	$K_p$	% mol H
1000	$5.17 \times 10^{-18}$	0.00
2000	$2.65 \times 10^{-6}$	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.

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

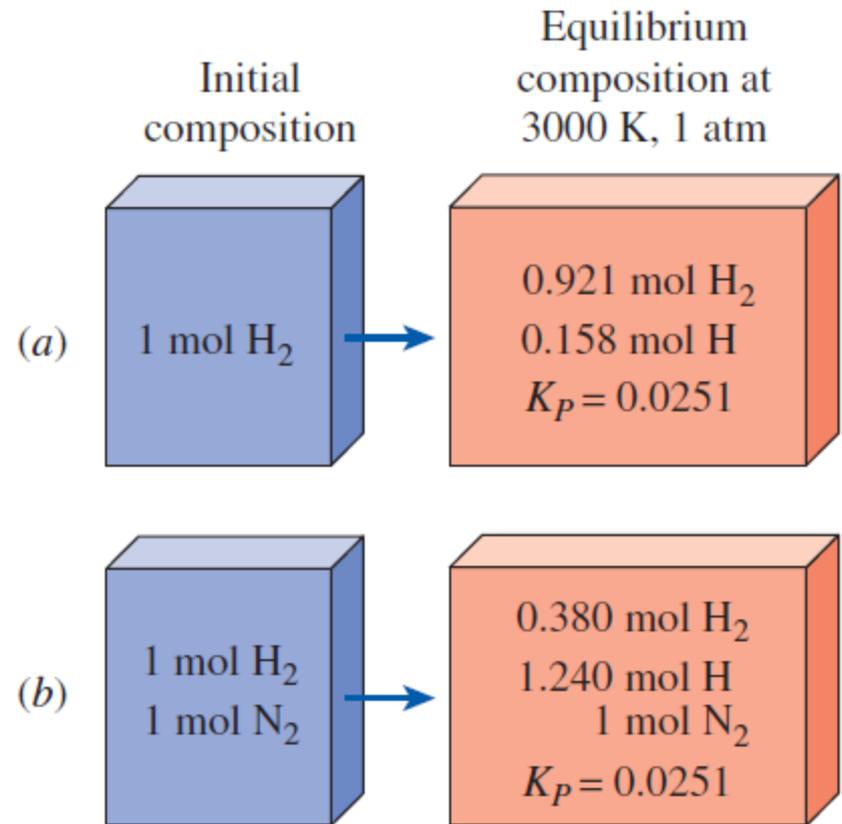
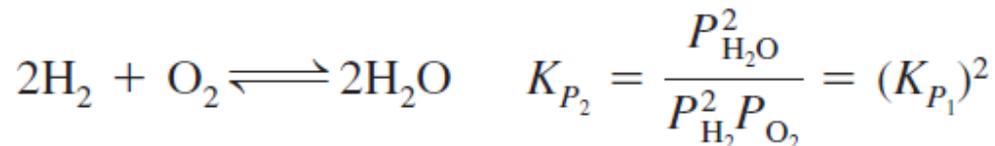
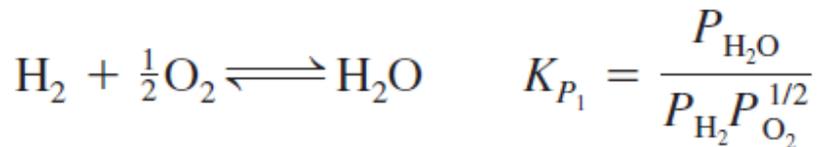
**5. The presence of inert gases affects the equilibrium composition**

**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  $N_{\text{total}}$  includes inert gases.

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

**6. When the stoichiometric coefficients are doubled, the value of  $K_P$  is squared.** For example,



**FIGURE 16–10**

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

**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, and at even higher temperatures atoms start to lose electrons and ionize.

**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. When the right catalyst is used, the reaction goes to completion rather quickly to the predicted value.



$$K_P = \frac{N_{\text{H}^+}^{v_{\text{H}^+}} N_{e^-}^{v_{e^-}}}{N_{\text{H}}^{v_{\text{H}}}} \left( \frac{P}{N_{\text{total}}} \right)^{\Delta v}$$

where

$$N_{\text{total}} = N_{\text{H}} + N_{\text{H}^+} + N_{e^-}$$

$$\Delta v = v_{\text{H}^+} + v_{e^-} - v_{\text{H}}$$

$$= 1 + 1 - 1$$

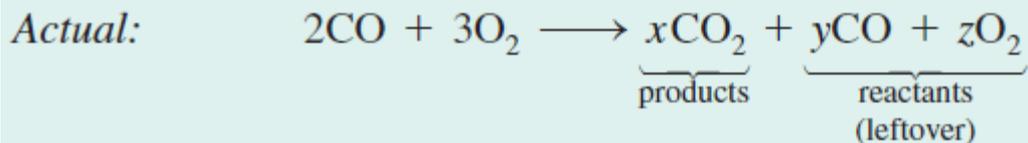
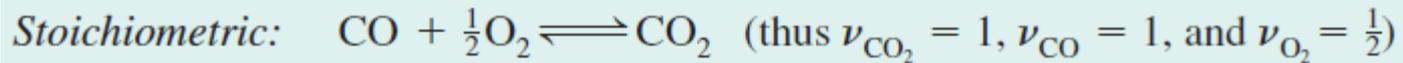
$$= 1$$

### FIGURE 16–11

Equilibrium-constant relation for the ionization reaction of hydrogen.

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

A mixture of 2 kmol of CO and 3 kmol of O<sub>2</sub> is heated to 2600 K at a pressure of 304 kPa. Determine the equilibrium composition, assuming the mixture consists of CO<sub>2</sub>, CO, and O<sub>2</sub> (Fig. 16-12).

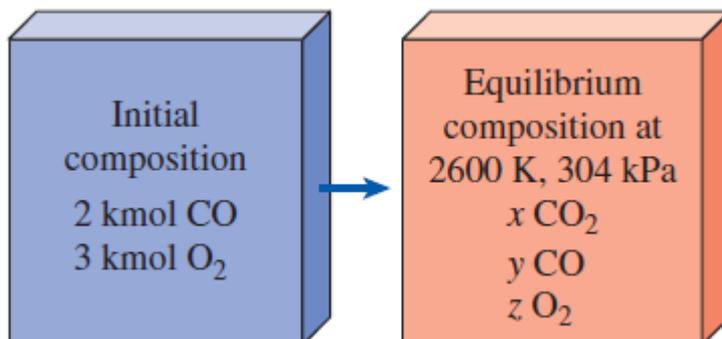


*C balance:*  $2 = x + y$  or  $y = 2 - x$

*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.

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

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

$$x = 1.906$$

$$y = 2 - x = 0.094$$

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



# CHEMICAL EQUILIBRIUM FOR SIMULTANEOUS REACTIONS

Most practical chemical reactions involve two or more reactions that occur simultaneously. 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.

A reacting system at a specified temperature and pressure achieves chemical equilibrium when its Gibbs function reaches a minimum value, that is,  $(dG)_{T,P} = 0$ .

When two or more reactions are involved, this condition is satisfied only when  $(dG)_{T,P} = 0$  for each reaction.

Composition:  $\text{CO}_2, \text{CO}, \text{O}_2, \text{O}$

No. of components: 4

No. of elements: 2

No. of  $K_p$  relations needed:  $4 - 2 = 2$

## 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.

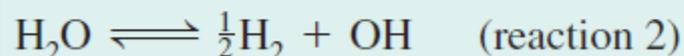
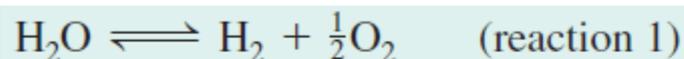
## EXAMPLE 16–5 Equilibrium Composition for Simultaneous Reactions

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).



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

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

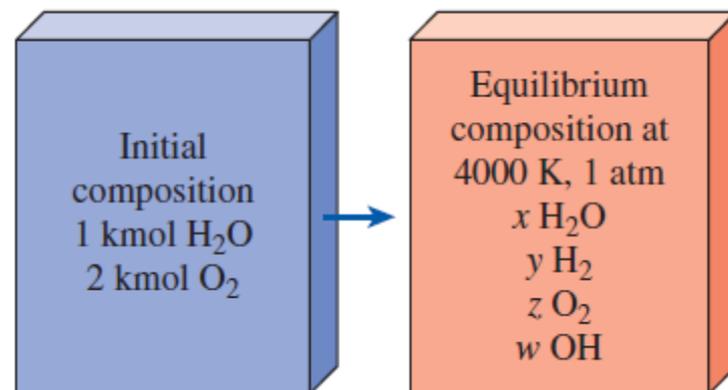


$$\ln K_{P_1} = -0.542 \longrightarrow K_{P_1} = 0.5816$$

$$\ln K_{P_2} = -0.044 \longrightarrow K_{P_2} = 0.9570$$

$$K_{P_1} = \frac{N_{\text{H}_2}^{\nu_{\text{H}_2}} N_{\text{O}_2}^{\nu_{\text{O}_2}}}{N_{\text{H}_2\text{O}}^{\nu_{\text{H}_2\text{O}}}} \left( \frac{P}{N_{\text{total}}} \right)^{\nu_{\text{H}_2} + \nu_{\text{O}_2} - \nu_{\text{H}_2\text{O}}}$$

$$K_{P_2} = \frac{N_{\text{H}_2}^{\nu_{\text{H}_2}} N_{\text{OH}}^{\nu_{\text{OH}}}}{N_{\text{H}_2\text{O}}^{\nu_{\text{H}_2\text{O}}}} \left( \frac{P}{N_{\text{total}}} \right)^{\nu_{\text{H}_2} + \nu_{\text{OH}} - \nu_{\text{H}_2\text{O}}}$$



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

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

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

$$x = 0.271 \quad y = 0.213$$

$$z = 1.849 \quad w = 1.032$$

$$\mathbf{0.271\text{H}_2\text{O} + 0.213\text{H}_2 + 1.849\text{O}_2 + 1.032\text{OH}} \quad 18$$

# VARIATION OF $K_P$ WITH TEMPERATURE

$$\ln K_P = -\frac{\Delta G^*(T)}{R_u T} \quad \text{the equilibrium constant } K_P \text{ of an ideal gas}$$

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

$$\frac{d(\ln K_P)}{dT} = \frac{\Delta H^*(T)}{R_u T^2} = \frac{\bar{h}_R(T)}{R_u T^2} \quad \text{van't Hoff equation}$$

where  $\bar{h}_R(T)$  is the enthalpy of reaction at temperature  $T$ .

Taking  $\bar{h}_R$  constant and integrating

$$\ln \frac{K_{P_2}}{K_{P_1}} \cong \frac{\bar{h}_R}{R_u} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

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	$1.41 \times 10^5$

This equation provides a means of calculating the  $\bar{h}_R$  of a reaction from a knowledge of  $K_P$ , which is easier to determine. Also, it shows that exothermic reactions such as combustion processes are less complete at higher temperatures since  $K_P$  decreases with temperature for such reactions.

Reaction: $C + O_2 \rightarrow CO_2$	
<u>T, K</u>	<u><math>K_p</math></u>
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.

$$\ln \frac{K_{P_2}}{K_{P_1}} \cong \frac{\bar{h}_R}{R_u} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Exothermic reactions such as combustion processes are less complete at higher temperatures since  $K_p$  decreases with temperature for such reactions.

**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  $\text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O}$  at 2000 K, using (a) enthalpy data and (b)  $K_p$  data.

$$\begin{aligned}\bar{h}_R &= \sum N_p(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_p - \sum N_r(\bar{h}_f^\circ + \bar{h} - \bar{h}^\circ)_r \\ &= N_{\text{H}_2\text{O}}(\bar{h}_f^\circ + \bar{h}_{2000\text{ K}} - \bar{h}_{298\text{ K}})_{\text{H}_2\text{O}} - N_{\text{H}_2}(\bar{h}_f^\circ + \bar{h}_{2000\text{ K}} - \bar{h}_{298\text{ K}})_{\text{H}_2} \\ &\quad - N_{\text{O}_2}(\bar{h}_f^\circ + \bar{h}_{2000\text{ K}} - \bar{h}_{298\text{ K}})_{\text{O}_2}\end{aligned}$$

$$\begin{aligned}\bar{h}_R &= (1 \text{ kmol H}_2\text{O})[(-241,820 + 82,593 - 9904) \text{ kJ/kmol H}_2\text{O}] \\ &\quad - (1 \text{ kmol H}_2)[(0 + 61,400 - 8468) \text{ kJ/kmol H}_2] \\ &\quad - (0.5 \text{ kmol O}_2)[(0 + 67,881 - 8682) \text{ kJ/kmol O}_2] \\ &= \mathbf{-251,663 \text{ kJ/kmol}}\end{aligned}$$

(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

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

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%.

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 if the temperature or the pressure is changed.

Therefore, we examine phase equilibrium at a specified temperature and pressure.

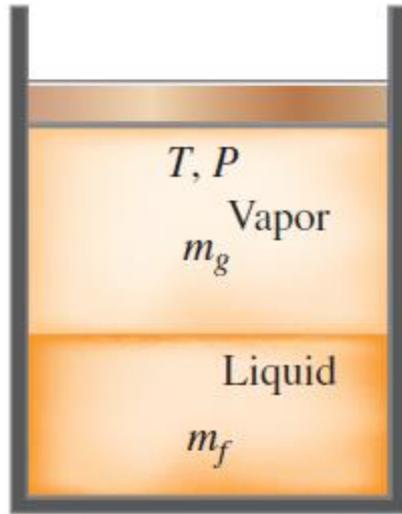
## PHASE EQUILIBRIUM



**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.

# Phase Equilibrium for a Single-Component System



**FIGURE 16–18**

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

The total Gibbs function of the mixture in the figure is

$$G = m_f g_f + m_g g_g$$

If during a disturbance a differential amount of liquid  $dm_f$  evaporates at constant  $T$  and  $P$ ,

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

At equilibrium,  $(dG)_{T,P} = 0$ . Also from the conservation of mass,  $dm_g = -dm_f$ . Substituting,

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

which must be equal to zero at equilibrium. It yields

$$g_f = g_g$$

The two phases of a pure substance are in equilibrium when each phase has the same value of specific Gibbs function.

At the triple point, the specific Gibbs functions of all three phases are equal to each other. The Gibbs function difference is the driving force for phase change. 23

### 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

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**:

$$IV = C - PH + 2$$

IV = number of independent variables

C = number of components

PH = number of phases present in equilibrium.

**Example 1:** At the triple point, PH = 3 and thus IV = 0. That is, none of the properties of a pure substance at the triple point can be varied.

**Example 2:** Based on this rule, two independent intensive properties need to be specified to fix the equilibrium state of a pure substance in a single phase

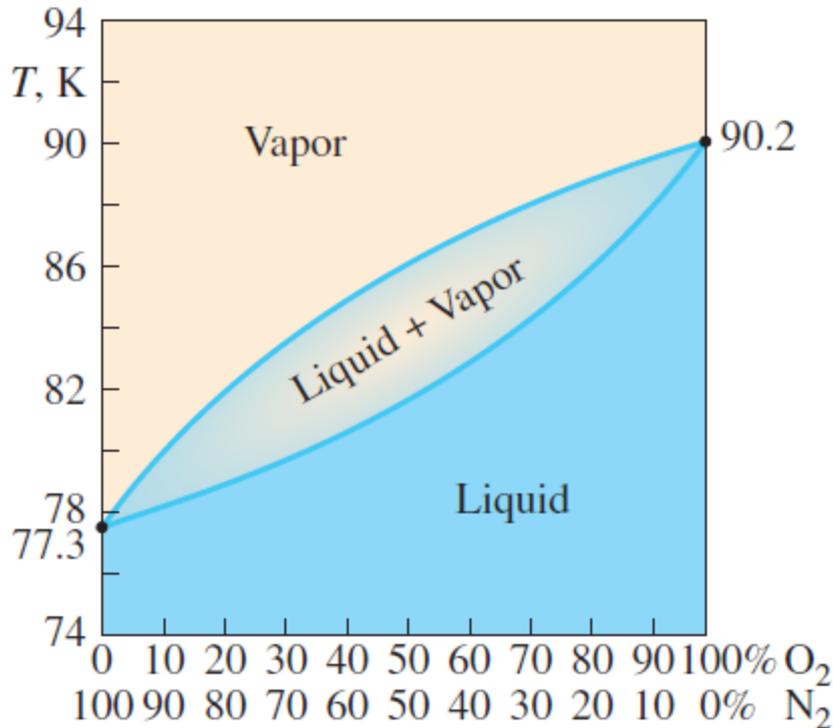


**FIGURE 16–19**

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

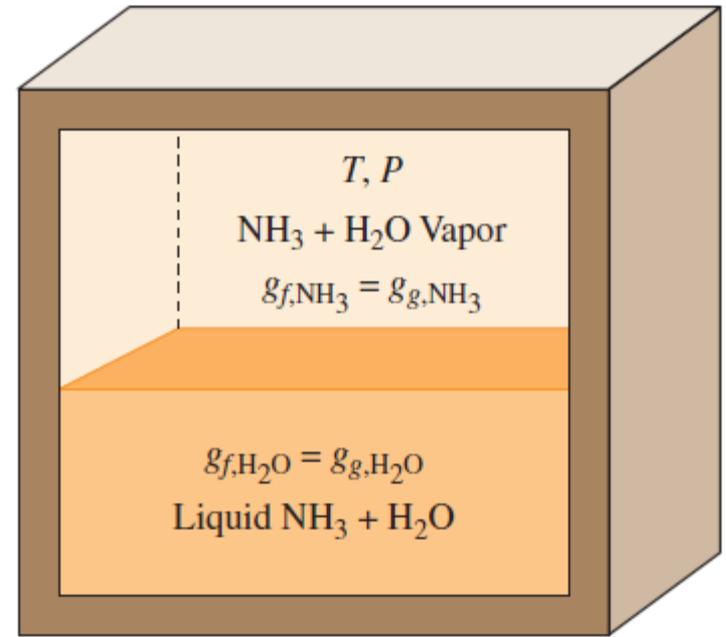
# Phase Equilibrium for a Multicomponent System

For the two phases of a two-component system, the mole fraction of a component is different in different phases. On the diagram shown, 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.



**FIGURE 16-21**

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



**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.

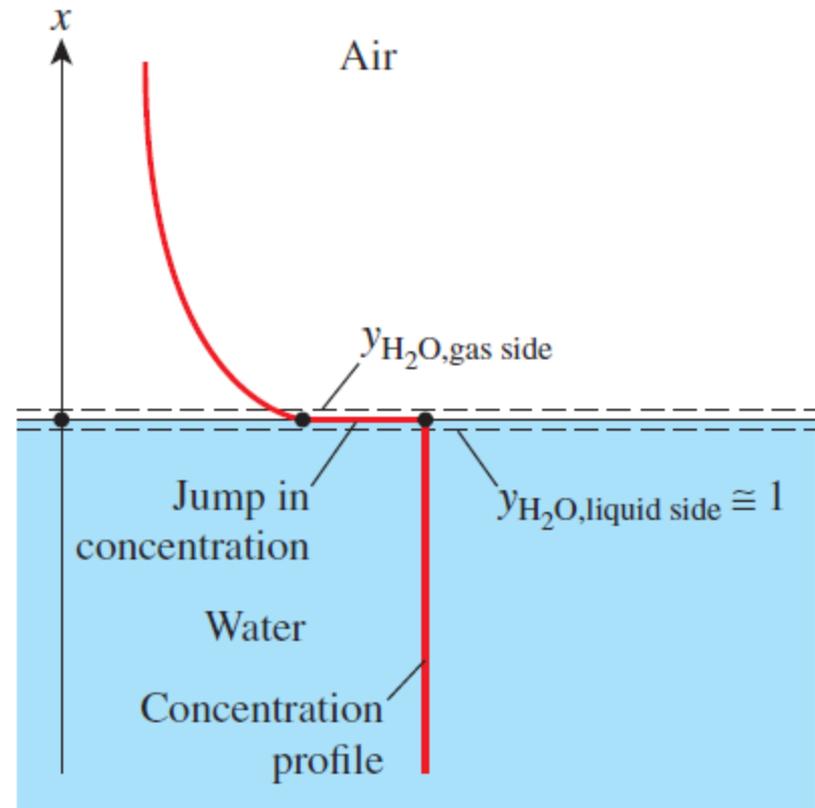
At a given temperature, only a certain amount of solid can be dissolved in a liquid, and the solubility of the solid in the liquid is determined from the requirement that thermodynamic equilibrium exists between the solid and the solution at the interface.

**Solubility:** The maximum amount of solid that can be dissolved in a liquid at a specified temperature.

**Example:** The solubility of salt (NaCl) in water at 310 K is 36.5 kg per 100 kg of water (Table 16-1). Therefore, the mass fraction of salt in the saturated brine is simply

$$mf_{\text{salt,liquid side}} = \frac{m_{\text{salt}}}{m} = \frac{36.5 \text{ kg}}{(100 + 36.5) \text{ kg}} = 0.267$$

whereas the mass fraction of salt in the pure solid salt is  $mf = 1.0$ .



**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	<i>Solute</i>	
	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

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

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

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.

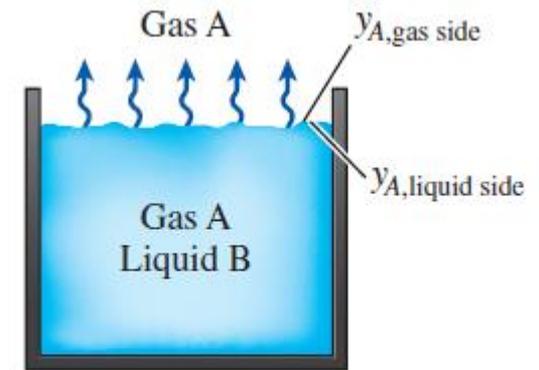
**TABLE 16-2**

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, 1995, 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

### From the table and Henry's law:

1. The concentration of a gas dissolved in a liquid is inversely proportional to Henry's constant.
2. The Henry's constant increases (and thus the fraction of a dissolved gas in the liquid decreases) with increasing temperature.
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 (e.g., the carbonation of soft drinks with CO<sub>2</sub> gas).



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

or

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

or

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

**FIGURE 16-23**

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

When the gas is highly soluble in the liquid (or solid), such as ammonia in water, 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

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

$P_{i,\text{sat}}(T)$  = the *saturation pressure* of the species *i* at the interface temperature  
 $P_{\text{total}}$  = the *total pressure* on the gas phase side

The molar density of the gas species *i* in the solid at the interface is proportional to the *partial pressure* of the species *i* in the gas on the gas side of the interface and is expressed as

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

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.

**TABLE 16-3**

Solubility of selected gases and solids (from Barrer, 1941)

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

$\mathcal{S}$			
Gas	Solid	$T$ , K	kmol/m <sup>3</sup> ·bar
O <sub>2</sub>	Rubber	298	0.00312
N <sub>2</sub>	Rubber	298	0.00156
CO <sub>2</sub>	Rubber	298	0.04015
He	SiO <sub>2</sub>	298	0.00045
H <sub>2</sub>	Ni	358	0.00901

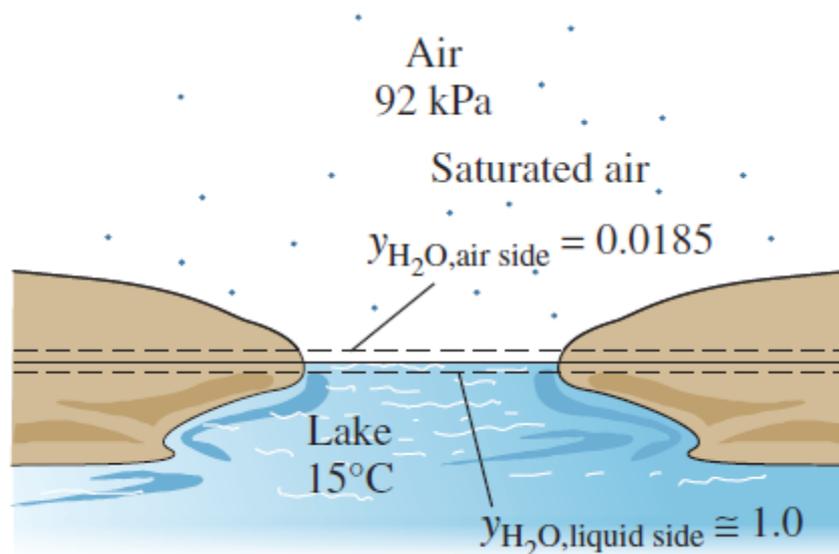
## EXAMPLE 16–8 Mole Fraction of Water Vapor Just over a Lake

Determine the mole fraction of the water vapor at the surface of a lake whose temperature is 15°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.

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

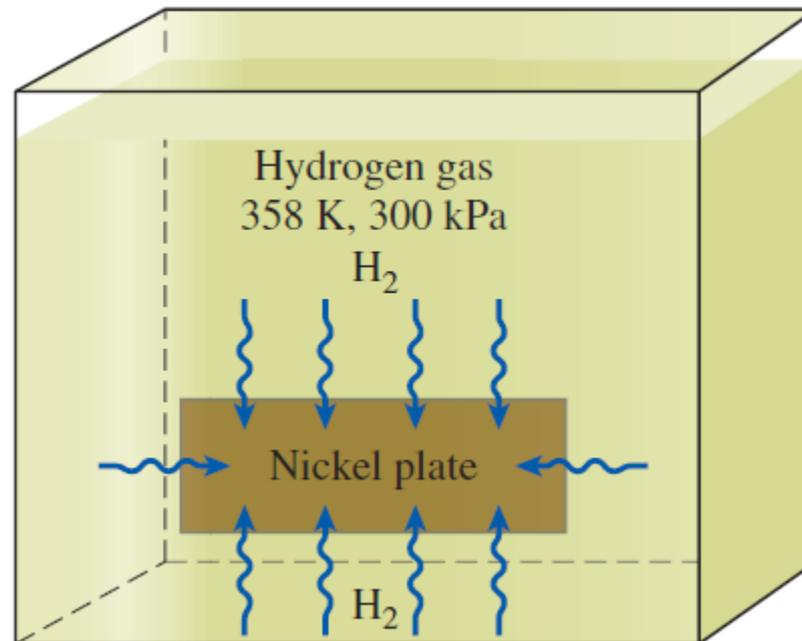
$$y_v = \frac{P_v}{P} = \frac{1.7057 \text{ kPa}}{92 \text{ kPa}} = \mathbf{0.0185 \text{ or } 1.85 \text{ percent}}$$

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



**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).

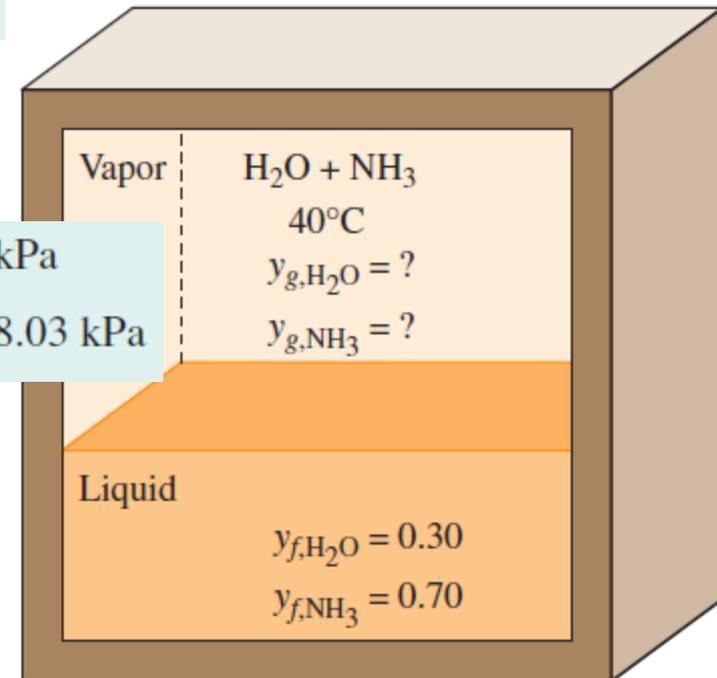


$$\begin{aligned}\bar{\rho}_{\text{H}_2, \text{solid side}} &= \mathcal{S} \times P_{\text{H}_2, \text{gas side}} \\ &= (0.00901 \text{ kmol/m}^3 \cdot \text{bar})(3 \text{ bar}) = \mathbf{0.027 \text{ kmol/m}^3}\end{aligned}$$

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

### 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.



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

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

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

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

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

# Summary

- Criterion for chemical equilibrium
- The equilibrium constant for ideal-gas mixtures
- Some remarks about the  $K_p$  of ideal-gas mixtures
- Chemical equilibrium for simultaneous reactions
- Variation of  $K_p$  with temperature
- Phase equilibrium
  - ✓ Phase equilibrium for a single-component system
  - ✓ The phase rule
  - ✓ Phase equilibrium for a multicomponent system