The right-hand sides of these equations are known from the thermodynamic data given previously. The solution is found to be

$$\xi_1 = 0.999998 \tag{12-66}$$

$$\xi_2 = 1.528 \times 10^{-6} \tag{12-67}$$

$$\xi_3 = 1.07 \times 10^{-12} \tag{12-68}$$

With these results it is obvious that the silane is almost completely converted to solid silicon and hydrogen.

In this example the only solid phase is *elemental* silicon; as a consequence, the analysis of solid species is trivial. In CVD we often deposit solid *compounds* on substrates which themselves are compounds, such as SiO_2. We turn then to a more complex example in order to see how this is handled.

Example 12-2.4 Tungsten CVD on silicon oxide. Tungsten is an important material for the formation of conducting films on selected regions of silicon and its oxide. A common source material is the gas-phase metal halide, tungsten hexafluoride (WF_6). An important issue is the potential for reactions that do not yield tungsten CVD.

Most often, tungsten is grown from a gas-phase mixture of hydrogen and tungsten hexafluoride with a large excess of hydrogen. The reaction stoichiometry is given by

$$3H_2 + WF_6 \rightarrow W + 6HF \tag{12-69}$$

Such a reaction would lead to tungsten deposition (metallization) on an inert surface. However, SiO_2 is not inert to WF_6, and a possible stoichiometry is

$$2H_2 + 2WF_6 + 3SiO_2 \rightarrow 3SiF_4 + 2WO_2 + 2H_2O \tag{12-70}$$

In this case, the oxide is actually *etched*; tungsten is not deposited but is incorporated in the oxide as WO_2.

An *equilibrium* thermodynamic analysis can tell us the maximum possible degree to which these reactions could proceed under a given set of conditions. By such an analysis we could select a set of operating conditions that promote the desired reaction. For example, we would like to know how to promote tungsten deposition on SiO_2 while avoiding the etching of the oxide, and the incorporation of WO_2 in the oxide.

The chemistry of this system seems quite complex. We have five elements: (H, F, O, Si, and W) and a large number of species. In the gas phase we must certainly consider the set (H_2, WF_6, SiF_4, HF, H_2O); solid species that must be considered include SiO_2, WO_2, and W. We will label these compounds and write the **A** matrix as

$$\begin{array}{c|cccccccc}
 & n_1 & n_2 & n_3 & n_4 & n_5 & n_6 & n_7 & n_8 \\
 & H_2 & WF_6 & SiO_2 & HF & H_2O & SiF_4 & WO_2 & W \\
\hline
H & 2 & 0 & 0 & 1 & 2 & 0 & 0 & 0 \\
F & 0 & 6 & 0 & 1 & 0 & 4 & 0 & 0 \\
O & 0 & 0 & 2 & 0 & 1 & 0 & 2 & 0 \\
Si & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\
W & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 1
\end{array}$$

The ν vectors follow from the solution to Eq. 12-34 and are found to be

$$\nu_1 = (\ 0 \quad 0 \quad -1 \quad -4 \quad +2 \quad 1 \quad 0 \quad 0)^T \tag{12-71}$$

$$\nu_2 = (-1 \quad -1 \quad 0 \quad 6 \quad -2 \quad 0 \quad 1 \quad 0)^T \tag{12-72}$$

$$\nu_3 = (-3 \quad -1 \quad 0 \quad 6 \quad 0 \quad 0 \quad 0 \quad 1)^T \tag{12-73}$$

We find that there are *three* ν vectors, and hence three independent stoichiometric equations for this system. By writing Eq. 12-35 for each ν vector in turn, and replacing the a_{ki} by the corresponding chemical formulas, we find the following stoichioimetric equations:

$$0H_2 + 0WF_6 - 1SiO_2 - 4HF + 2H_2O + 1SiF_4 + 0WO_2 + 0W = 0 \tag{12-74}$$

or

$$SiO_2 + 4HF = 2H_2O + SiF_4 \tag*{(12-75)†}$$

$$-1H_2 - 1WF_6 + 0SiO_2 + 6HF - 2H_2O + 0SiF_4 + 1WO_2 + 0W = 0 \tag{12-76}$$

or

$$H_2 + WF_6 + 2H_2O = 6HF + WO_2 \tag{12-77}$$

$$-3H_2 - 1WF_6 + 0SiO_2 + 6HF + 0H_2O + 0SiF_4 + 0WO_2 + 1W = 0 \tag{12-78}$$

or

$$3H_2 + WF_6 = 6HF + W \tag{12-79}$$

Note that this formal matrix procedure gives us the expected Eq. 12-69, *not* Eq. 12-70. If we had assumed that the only reactions were given by Eqs. 12-69 and 12-70, and then proceeded with the free energy minimization, we would have obtained a physically unrealizable result.

We have discovered that for this chemical system there are *three* extent of reaction variables ξ_i that we must obtain using the energy minimization principle (Eq. 12-54), which leads to

$$-\mu_3 - 4\mu_4 + 2\mu_5 + \mu_6 = 0 \tag{12-80}$$

$$-\mu_1 - \mu_2 + 6\mu_4 - 2\mu_5 + \mu_7 = 0 \tag{12-81}$$

$$-3\mu_1 - \mu_2 + 6\mu_4 + \mu_8 = 0 \tag{12-82}$$

The composition of the equilibrium mixture then follows from the set of mole numbers $\mathbf{n}_i$:

$$H_2: \quad n_1 = n_1^\circ - \xi_2 - 3\xi_3 \tag{12-83}$$

$$WF_6: \quad n_2 = n_2^\circ - \xi_2 - \xi_3 \tag{12-84}$$

$$SiO_2: \quad n_3 = n_3^\circ - \xi_1 \tag{12-85}$$

$$HF: \quad n_4 = n_4^\circ - 4\xi_1 + 6\xi_2 + 6\xi_3 \tag{12-86}$$

$$H_2O: \quad n_5 = n_5^\circ + 2\xi_1 - 2\xi_2 \tag{12-87}$$

$$SiF_4: \quad n_6 = n_6^\circ + \xi_1 \tag{12-88}$$

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† Remember that $\nu_{ij} > 0$ corresponds to *products*.

$$\text{WO}_2: \quad n_7 = n_7^\circ + \xi_2 \tag{12-89}$$

$$\text{W}: \quad n_8 = n_8^\circ + \xi_3 \tag{12-90}$$

To implement Eqs. 12-80–82 we must write the chemical potentials for each species. We use Eqs. 12-3 and 12-4 for all gas-phase species. We will take $\mu_i = \mu_i^\circ$ for the three solid species (we define the activity as unity for all solids) and we make note of the fact that the chemical potential of the element in its reference state (in this example solid tungsten) is, by definition, zero. These ideas lead to the following equations:

$$\frac{n n_5^2 n_6}{n_4^4} = P \exp\left(\frac{-\mu_3^\circ - 4\mu_4^\circ + 2\mu_5^\circ + \mu_6^\circ}{R_G T}\right) \tag{12-91}$$

$$\frac{n_4^6}{n_1 n_2 n_5^2 n^2} = P^{-2} \exp\left(\frac{-\mu_2^\circ + 6\mu_4^\circ - 2\mu_5^\circ + \mu_7^\circ}{R_G T}\right) \tag{12-92}$$

$$\frac{n_4^6}{n_1^3 n_2 n^2} = P^{-2} \exp\left(\frac{-\mu_2^\circ + 6\mu_4^\circ}{R_G T}\right) \tag{12-93}$$

(Note that $\mu_1^\circ = \mu_8^\circ = 0$ and n_3, n_7, n_8 do not appear on the left-hand sides because they refer to *solid*, not gas-phase, species.) The total number of moles in the gas phase is

$$n = n_1^\circ + n_2^\circ - \xi_1 + 2\xi_2 + 2\xi_3 \tag{12-94}$$

(Only species 1 and 2 are in the initial gas phase.)

When Eqs. 12-83–90 and 12-94 are inserted into Eqs. 12-91–93 the result is a set of three nonlinear algebraic equations for the extent of reaction variables ξ_1, ξ_2, and ξ_3. Once a specific temperature and pressure are selected we can calculate a numerical value for the right-hand sides of these three equations.

As an example, at $T = 700$ K we find the following data [all in kcal/(g·mol)]:

H_2: $\mu_1^\circ = 0$

WF_6: $\mu_2^\circ = -362$

SiO_2: $\mu_3^\circ = -187$

HF: $\mu_4^\circ = -66.2$

H_2O: $\mu_5^\circ = -50$ (note that this is gaseous, not liquid, H_2O)

SiF_4: $\mu_6^\circ = -362$

WO_2: $\mu_7^\circ = -110$

W: $\mu_8^\circ = 0$ (elemental W)

We multiply all μ° by 4184 to convert to units of J/(g·mol), and we use $R_G = 8.314$ J/(g·mol·K).

We take a pressure of $P = 0.75$ torr for this example. Since P must be in units of atm we have $P = 9.87 \times 10^{-4}$ atm.

A numerical solution for ξ_1, ξ_2, ξ_3 can be carried out, and for this example the solution is

$$\xi_1 = 0.916 \tag{12-95}$$

$$\xi_2 = 0.5095 \tag{12-96}$$

$$\xi_3 = 0.4905 \tag{12-97}$$

for the initial mixture conditions of

$$n_1^\circ = 40 \text{ g}\cdot\text{mol H}_2$$

$$n_2^\circ = 1 \text{ g}\cdot\text{mol WF}_6$$

$$n_3^\circ = 1.5 \text{ g}\cdot\text{mol SiO}_2$$

(We will comment subsequently on this choice of n_3°.)

As we suggested at the beginning of this example, an important practical question is whether tungsten is actually deposited on the oxide. If we examine the results presented thus far, we see that for each mole n_2° of tungsten initially exposed to the SiO_2 surface (as WF_6), we will deposit WO_2 and W in the amounts (ξ_2) mol WO_2 and (ξ_3) mol W. These are important measures of the performance of the system, and we can calculate them as a function of operating conditions. For example, Figure 12-1 shows the equilibrium yield of solid product, as moles of solid per mole of tungsten hexafluoride feed, as a function of temperature, at a pressure of 0.75 torr. If our goal is to deposit W in preference to the oxide, we must operate at temperatures in excess of 800 K. Above that temperature there is no expectation of WO_2 deposition.

From Eq. 12-75 we see that there is a possibility that HF will etch SiO_2. In Figure 12-1 we also plot the moles of SiO_2 (ξ_1) etched per mole of WF_6 feed, as a function of temperature.

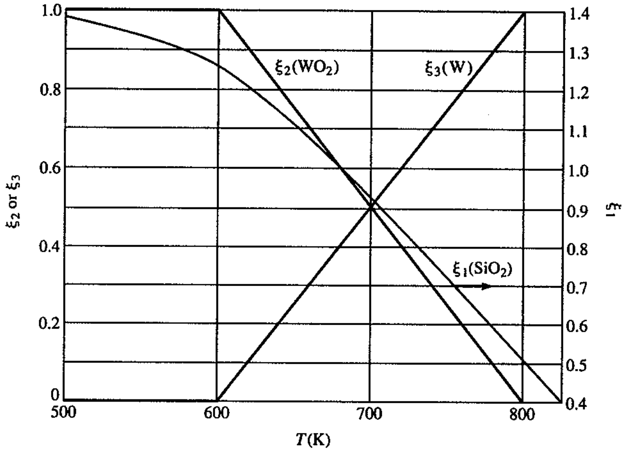

FIGURE 12-1
Predicted equilibrium yield of solid product (moles of solid per mole of tungsten hexafluoride in the feed gas) vs. T, at a pressure of 0.75 torr. Also shown (labeled ξ_1) is the moles of solid oxide *etched* by the fluoride.