

The last row gives the mole fractions in the *gas* phase. Since carbon is present only in the solid phase, its moles are not included in the determination of the total moles of gas-phase species:

$$n_{\text{tot}}^{\text{gas}} = 0.7 - \xi + 0.15 + 2\xi + 0.15 = 1 + \xi.$$

This is the number of moles used in the calculation of the gas-phase mol fractions. The equilibrium condition involves only the gas-phase reactants, methane and hydrogen. Neglecting the fugacity coefficients, the equilibrium reads

$$\text{CH}_4 \quad \frac{y_{\text{H}_2}^2}{y_{\text{N}_2}} \left(\frac{P}{P^\circ} \right) = K(T).$$

Expressing the mol fractions in terms of ξ , this equation becomes

$$\text{remove "2"} \quad \frac{2(0.15 + 2\xi)^2}{(0.7 - \xi)(1 + \xi)} = K(T) \left(\frac{P}{P} \right), \quad \text{P0 in the numerator, P in the denominator}$$

and by expanding we obtain a quadratic equation in ξ :

$$0.0225 - \frac{0.7P}{P_0} K(T) + \xi \left(0.6 + \frac{0.3P}{P_0} K(T) \right) + \xi^2 \left(4 + \frac{P}{P_0} K(T) \right) = 0 \quad [\text{A}]$$

This equation is to be solved for the unknown extent of the reaction.

Numerical substitutions. The standard enthalpy and Gibbs free energy of the reaction are $\Delta H_{298}^\circ = -74,520$ J/mol and $\Delta G_{298}^\circ = -50,450$ J/mol, respectively. The equilibrium constant at 298.15 K is

$$K_{298} = 1.44894 \times 10^{-9} \quad \text{remove minus sign}$$

The equilibrium constant at T will be calculated by the simplified expression in eq. (14.36). At 600 K and at 800 K we find,

$$K_{600} = 5.362 \times 10^{-3}, \quad K_{800} = 0.2245.$$

Calculation at 600 K. With $K = 5.362 \times 10^{-3}$ eq. [A] becomes

$$0.0187465 + 0.601609\xi + 4.00536\xi^2 = 0,$$

whose two roots are

$$\xi = -0.10608, \quad \xi = -0.044121.$$

Both roots are negative, which implies the reverse reaction is taking place. However there is no carbon present initially, so the reverse reaction cannot actually occur. We conclude that no carbon will be deposited at 600 Kelvin.

Calculation at 800 K. With $K = 0.2245$ eq. [A] becomes

$$-0.134674 + 0.66736\xi + 4.22453\xi^2 = 0,$$

whose roots are

$$\xi = -0.274224, \quad \xi = 0.116252.$$

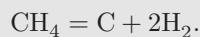
The positive root corresponds to forward reaction and we conclude that carbon deposition will occur at 800 K. The resulting gas-phase mol reactions are

$$y_{\text{CH}_4} = 0.523, \quad y_{\text{C}} = 0, \quad y_{\text{H}_2} = 0.343, \quad y_{\text{N}_2} = 0.134.$$

Comments At 600 K there is no deposition of carbon. This corresponds to the reaction going quantitatively from left (products) to right (reactants). Normally, a reversible reaction will shift from left to right until the mol fractions adjust to the values that satisfy the condition for chemical equilibrium. However, when a solid is involved, its mol fraction does not appear in the equilibrium constant, and this makes it possible to reach an equilibrium state that the solid is fully consumed.

Example 14.18: Phase Diagram for Carbon Deposition

Use the data of Example 14.8 to create a pressure-temperature graph and show the region where carbon deposition is expected according to the reaction



Solution In the previous example we obtained the following equation for the extent of reaction:

$$0.0225 - \frac{0.7P}{P_0} K(T) + \xi \left(0.6 + \frac{0.3P}{P_0} K(T) \right) + \xi^2 \left(4 + \frac{P}{P_0} K(T) \right) = 0 \quad [\text{A}]$$

Deposition occurs if this equation has a positive root. Inspecting the coefficients of this quadratic polynomial we notice that the sum of the roots is always negative. This means that if the quadratic equation has real roots, at least one is always negative. Carbon deposition requires the presence of a positive root. In order to have a positive root, the constant term of the quadratic must be negative:

$$0.0225 - \frac{0.7P}{P_0} K(T) \leq 0 \quad \Rightarrow \quad P \geq 0.032143 \frac{P_0}{K(T)}.$$

The last inequality defines the region of the PT plane where deposition of carbon is thermodynamically feasible. This is plotted in Figure 14-4 with the shaded region marking the range of pressure and temperatures where deposition can occur.

Comments These results are specific to the composition of the methane/hydrogen/nitrogen mixture. If this composition changes, the phase diagram must be recalculated by repeating the calculations in Example 14.8.

14.17

PO in numerator
P in denominator

$P \leq P_0 K(T)$

New figure (to be supplied)

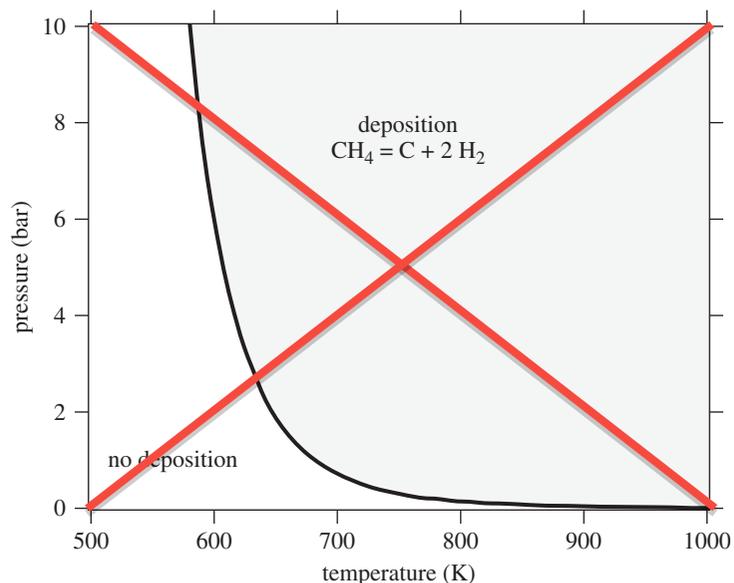
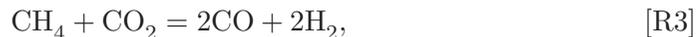
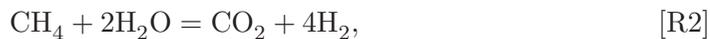


Figure 14-4: Phase diagram for carbon deposition according to the reaction $\text{CH}_4 = \text{C} + 2\text{H}_2$ (see Example 14.18).

14.9 Multiple Reactions

When multiple reactions take place, each reaction provides an equilibrium condition that may be used in the calculation of the final composition. However, it is not always obvious how many independent reactions are present. For example, in the reforming of methane by steam we may write the following four reactions that produce a mixture of carbon monoxide, carbon dioxide and hydrogen:



Notice that reaction R4 can be obtained by subtracting reaction R1 from R2. This means that at least one reaction in this system is not independent. A systematic method to determine the number of independent reactions is to begin with the matrix of stoichiometric coefficients of all components that appear in these reactions.