Example 13.1 For a system in which the following reaction occurs,

$$\overset{(1)}{CH_4} + \overset{(2)}{H_2O} \rightarrow \overset{(3)}{CO} + \overset{(4)}{3H_2}$$

assume there are present initially 2 mol CH_4, 1 mol H_2O, 1 mol CO, and 4 mol H_2. Determine expressions for the mole fractions y_i as functions of ε.

$$y_i = \frac{n_{io} + \gamma_i \varepsilon}{n_o + \gamma \varepsilon}$$

$$n_{10} = 2, \quad n_{20} = 1, \quad n_{30} = 1 \;\&\; n_{40} = 4$$

$$\gamma_1 = -1, \quad \gamma_2 = -1, \quad \gamma_3 = +1 \;\&\; \gamma_4 = +3$$

$$\gamma = (-1) + (-1) + (1) + (3) = 2$$

$$n_o = 2 + 1 + 1 + 4 = 8$$

$$y_1 = \frac{2 + (-1)\varepsilon}{8 + 2\varepsilon} = \frac{2 - \varepsilon}{8 + 2\varepsilon}, \quad y_2 = \frac{1 - \varepsilon}{8 + 2\varepsilon}$$

$$y_3 = \frac{1 + \varepsilon}{8 + 2\varepsilon} \qquad y_4 = \frac{4 + 3\varepsilon}{8 + 2\varepsilon}$$

Example 13.2 Consider a vessel which initially contains only n_0 moles of water vapor. If decomposition occurs according to the reaction

$$\overset{(1)}{H_2O} \rightarrow \overset{(2)}{H_2} + \overset{(3)}{\tfrac{1}{2}O_2} \qquad \gamma = \frac{1}{2}$$

find expressions which relate the number of moles and the mole fraction of each chemical species to the reaction coordinate ε.

$$n_i = n_{io} + \overset{\gamma_i}{\varepsilon} \qquad y_i = \frac{n_{io} + \gamma_i \varepsilon}{n_o + \gamma \varepsilon}$$

for this problem $(n_{10} = n_o$

$$n_1 = n_o - \varepsilon \qquad y_1 = \frac{n_o - \varepsilon}{n_o + \frac{1}{2}\varepsilon}$$

$$n_2 = \varepsilon \qquad y_2 = \frac{\varepsilon}{n_o + \frac{1}{2}\varepsilon}$$

$$n_3 = \frac{1}{2}\varepsilon \qquad y_3 = \frac{\frac{1}{2}\varepsilon}{n_o + \frac{1}{2}\varepsilon}$$

Example 13.3 Consider a system in which the following reactions occur:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (2)$$

where the numbers (1) and (2) indicate the value of j, the reaction index. If there are present initially 2 mol CH_4 and 3 mol H_2O, determine expressions for the y_i as functions of ε_1 and ε_2.

SOLUTION The stoichiometric numbers $\nu_{i,j}$ can be arrayed as follows:

$i =$	CH_4	H_2O	CO	CO_2	H_2	
j						ν_j
1	−1	−1	1	0	3	2
2	−1	−2	0	1	4	2

Application of Eq. (13.7) now gives

$$y_{CH_4} = \frac{2 - \varepsilon_1 - \varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

$$y_{H_2O} = \frac{3 - \varepsilon_1 - 2\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

$$y_{CO} = \frac{\varepsilon_1}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

$$y_{CO_2} = \frac{\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

$$y_{H_2} = \frac{3\varepsilon_1 + 4\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$$

The composition of the system is a function of the independent variables ε_1 and ε_2.