EXAMPLE 13.10

$ORIGIN := 1$

First Reaction

$$\Delta H_f := \begin{pmatrix} -74.90 \\ -242 \\ -110.6 \\ 0 \end{pmatrix} \qquad \Delta G_f := \begin{pmatrix} -50.87 \\ -228.8 \\ -137.4 \\ 0 \end{pmatrix} \qquad \alpha := \begin{pmatrix} -1 \\ -1 \\ 1 \\ 3 \end{pmatrix}$$

$$a := \begin{pmatrix} 36.155 \\ 33.763 \\ 29.651 \\ 27.004 \end{pmatrix} \qquad b := \begin{pmatrix} -0.511 \\ -0.006 \\ -0.007 \\ 0.119 \end{pmatrix} \cdot 10^{-1} \qquad c := \begin{pmatrix} 2.215 \\ 0.224 \\ 0.183 \\ -0.241 \end{pmatrix} \cdot 10^{-4}$$

$$d := \begin{pmatrix} -1.824 \\ -0.100 \\ -0.094 \\ 0.215 \end{pmatrix} \cdot 10^{-7} \qquad e := \begin{pmatrix} 4.899 \\ 0.110 \\ 0.108 \\ -0.615 \end{pmatrix} \cdot 10^{-11}$$

$i := 1 .. 4$

$$\Delta G_{298} := \left[\sum_i \left(\alpha_i \cdot \Delta G_{f_i}\right)\right] \cdot 1000 \qquad \Delta H_{298} := \left[\sum_i \left(\alpha_i \cdot \Delta H_{f_i}\right)\right] \cdot 1000$$

$$\Delta a := \sum_i \left(a_i \cdot \alpha_i\right) \qquad \Delta b := \left[\sum_i \left(b_i \cdot \alpha_i\right)\right] \qquad \Delta c := \left[\sum_i \left(c_i \cdot \alpha_i\right)\right]$$

$$\Delta d := \left[\sum_i \left(d_i \cdot \alpha_i\right)\right] \qquad \Delta e := \left[\sum_i \left(e_i \cdot \alpha_i\right)\right]$$

$$\Lambda := \Delta a \cdot 298 + \frac{298^2 \cdot \Delta b}{2} + \frac{298^3 \cdot \Delta c}{3} + \frac{298^4 \cdot \Delta d}{4} + \frac{298^5 \cdot \Delta e}{5} - \Delta H_{298}$$

$$\Omega := (1 + \ln(298)) \cdot \Delta a + 298 \cdot \Delta b + \frac{298^2 \cdot \Delta c}{2} + \frac{298^3 \cdot \Delta d}{3} + \frac{298^4 \cdot \Delta e}{4} - \frac{\Delta H_{298} - \Delta G_{298}}{298}$$

$R := 8.314 \qquad T := 800$

$$K_{a1} := \exp\left[\frac{1}{R}\cdot\left(\Delta a\cdot \ln(T) + \frac{\Delta b}{2}\cdot T + \frac{\Delta c}{6}\cdot T^2 + \frac{\Delta d}{12}\cdot T^3 + \frac{\Delta e}{20}\cdot T^4 + \frac{\Lambda}{T} - \Omega\right)\right] = 0.031$$

Second Reaction

$$\Delta H_f := \begin{pmatrix} -74.90 \\ -242 \\ -393.8 \\ 0 \end{pmatrix} \qquad \Delta G_f := \begin{pmatrix} -50.87 \\ -228.8 \\ -394.6 \\ 0 \end{pmatrix} \qquad \alpha := \begin{pmatrix} -1 \\ -2 \\ 1 \\ 4 \end{pmatrix}$$

$$a := \begin{pmatrix} 36.155 \\ 33.763 \\ 29.268 \\ 27.004 \end{pmatrix} \qquad b := \begin{pmatrix} -0.511 \\ -0.006 \\ -0.224 \\ 0.119 \end{pmatrix}\cdot 10^{-1} \qquad c := \begin{pmatrix} 2.215 \\ 0.224 \\ 2.653 \\ -0.241 \end{pmatrix}\cdot 10^{-4}$$

$$d := \begin{pmatrix} -1.824 \\ -0.100 \\ -4.153 \\ 0.215 \end{pmatrix}\cdot 10^{-7} \qquad e := \begin{pmatrix} 4.899 \\ 0.110 \\ 20.057 \\ -0.615 \end{pmatrix}\cdot 10^{-11}$$

$i := 1 .. 4$

$$\Delta G_{298} := \left[\sum_i \left(\alpha_i\cdot \Delta G_{f_i}\right)\right]\cdot 1000 \qquad \Delta H_{298} := \left[\sum_i \left(\alpha_i\cdot \Delta H_{f_i}\right)\right]\cdot 1000$$

$$\Delta a := \sum_i \left(a_i\cdot\alpha_i\right) \qquad \Delta b := \left[\sum_i \left(b_i\cdot\alpha_i\right)\right] \qquad \Delta c := \left[\sum_i \left(c_i\cdot\alpha_i\right)\right]$$

$$\Delta d := \left[\sum_i \left(d_i\cdot\alpha_i\right)\right] \qquad \Delta e := \left[\sum_i \left(e_i\cdot\alpha_i\right)\right]$$

$$\Lambda := \Delta a\cdot 298 + \frac{298^2\cdot\Delta b}{2} + \frac{298^3\cdot\Delta c}{3} + \frac{298^4\cdot\Delta d}{4} + \frac{298^5\cdot\Delta e}{5} - \Delta H_{298}$$

$$\Omega := (1 + \ln(298))\cdot\Delta a + 298\cdot\Delta b + \frac{298^2\cdot\Delta c}{2} + \frac{298^3\cdot\Delta d}{3} + \frac{298^4\cdot\Delta e}{4} - \frac{\Delta H_{298} - \Delta G_{298}}{298}$$

$R := 8.314 \qquad T := 800$

$$K_{a2} := \exp\left[\frac{1}{R}\cdot\left(\Delta a\cdot\ln(T) + \frac{\Delta b}{2}\cdot T + \frac{\Delta c}{6}\cdot T^2 + \frac{\Delta d}{12}\cdot T^3 + \frac{\Delta e}{20}\cdot T^4 + \frac{\Lambda}{T} - \Omega\right)\right] = 0.096$$

Initial guess values

$\varepsilon_1 := 0.2$ $\quad\quad\quad$ $\varepsilon_2 := 0.5$

Given

$$\frac{\varepsilon_1\cdot(3\cdot\varepsilon_1 + 4\cdot\varepsilon_2)^3}{(1 - \varepsilon_1 - \varepsilon_2)\cdot(5 - \varepsilon_1 - 2\cdot\varepsilon_2)\cdot(6 + 2\cdot\varepsilon_1 + 2\cdot\varepsilon_2)^2} = \frac{K_{a1}}{4}$$

$$\frac{\varepsilon_2\cdot(3\cdot\varepsilon_1 + 4\cdot\varepsilon_2)^4}{(1 - \varepsilon_1 - \varepsilon_2)\cdot(5 - \varepsilon_1 - 2\cdot\varepsilon_2)^2\cdot(6 + 2\cdot\varepsilon_1 + 2\cdot\varepsilon_2)^2} = \frac{K_{a2}}{4}$$

$$\text{Find}(\varepsilon_1, \varepsilon_2) = \begin{pmatrix} 0.079 \\ 0.463 \end{pmatrix}$$