Problem 2-09 Parallel reactions, temperature dependence

Catalytic decomposition of formic acid in the gaseous phase can take place by these two reactions

(1) $HCOOH \rightarrow H_2O + CO$ and (2) $HCOOH \rightarrow H_2 + CO_2$.

The rate constants at the temperature of 510 K have these values:

$$k_1 = 4.7\cdot10^{-5}\ \mathrm{s^{-1}} \text{ and } k_2 = 2.5\cdot10^{-6}\ \mathrm{s^{-1}}.$$

Assuming that the activation energies, $E_1^* = 50.2$ kJ mol^{-1} and $E_2^* = 102.5$ kJ mol^{-1} are temperature independent, find such temperature at which the decomposition of formic acid gives an equimolar mixture of water vapour, carbon monoxide, hydrogen, and carbon dioxide

[T = 669.2 K]

Solution:

Temperature dependence of the rate constant k_1: $\ln\dfrac{k_{1\mathrm{b}}}{k_{1\mathrm{a}}} = \dfrac{E_1^*}{\boldsymbol{R}}\cdot\left(\dfrac{1}{T_\mathrm{a}} - \dfrac{1}{T_\mathrm{b}}\right)$

Temperature dependence of the rate constant k_2: $\ln\dfrac{k_{2\mathrm{b}}}{k_{2\mathrm{a}}} = \dfrac{E_2^*}{\boldsymbol{R}}\cdot\left(\dfrac{1}{T_\mathrm{a}} - \dfrac{1}{T_\mathrm{b}}\right)$

$$\ln\frac{k_{1\mathrm{b}}}{k_{1\mathrm{a}}} - \ln\frac{k_{2\mathrm{b}}}{k_{2\mathrm{a}}} = \frac{E_1^*}{\boldsymbol{R}}\cdot\left(\frac{1}{T_\mathrm{a}} - \frac{1}{T_\mathrm{b}}\right) - \frac{E_2^*}{\boldsymbol{R}}\cdot\left(\frac{1}{T_\mathrm{a}} - \frac{1}{T_\mathrm{b}}\right)$$

$$\ln\frac{k_{1\mathrm{b}}}{k_{1\mathrm{a}}}\cdot\frac{k_{2\mathrm{a}}}{k_{2\mathrm{b}}} = \frac{E_1^* - E_2^*}{\boldsymbol{R}}\cdot\left(\frac{1}{T_\mathrm{a}} - \frac{1}{T_\mathrm{b}}\right)$$

$$\Downarrow$$

$$\ln\left(\frac{k_{1\mathrm{b}}}{k_{2\mathrm{b}}}\right)\cdot\left(\frac{k_{2\mathrm{a}}}{k_{1\mathrm{a}}}\right)$$

At $T_\mathrm{a} = 510$ K $\qquad \dfrac{k_{1\mathrm{a}}}{k_{2\mathrm{a}}} = \dfrac{4.7\cdot10^{-5}}{2.5\cdot10^{-6}} = 18.8$

At $T_\mathrm{b} = ?$ $\qquad \dfrac{k_{1\mathrm{b}}}{k_{2\mathrm{b}}} = \dfrac{n_{H_2O}}{n_{H_2}} = \dfrac{n_{CO}}{n_{CO_2}} = 1$ (equimolar mixture: $c_{H2O} = c_{H2} = c_{CO} = c_{CO2}$)

$$\frac{1}{T_\mathrm{b}} = \frac{1}{T_\mathrm{a}} - \frac{\boldsymbol{R}}{(E_1^* - E_2^*)}\cdot\ln\left(\frac{k_{1\mathrm{b}}}{k_{2\mathrm{b}}}\right)\cdot\left(\frac{k_{2\mathrm{a}}}{k_{1\mathrm{a}}}\right)$$

$$= \frac{1}{510} - \frac{8.314}{(50200 - 102500)}\cdot\ln\left(\frac{2.5\cdot10^{-6}}{4.7\cdot10^{-5}}\cdot1\right)$$

$$= 1.960784\cdot10^{-3} - 4.66387\cdot10^{-4}$$

$$= 1.4944\cdot10^{-3}$$

$$T_\mathrm{b} = 669.17\ \mathrm{K}$$

or:

$k_{1\mathrm{a}} = 18.8\cdot k_{2\mathrm{a}}$: $\quad A_1\cdot\exp\left(-\dfrac{E_1^*}{\boldsymbol{R}T_\mathrm{a}}\right) = 18.8\cdot A_2\cdot\exp\left(-\dfrac{E_2^*}{\boldsymbol{R}T_\mathrm{a}}\right)$

$k_{1\mathrm{b}} = k_{2\mathrm{b}}$: $\quad A_1\cdot\exp\left(-\dfrac{E_1^*}{\boldsymbol{R}T_\mathrm{b}}\right) = A_2\cdot\exp\left(-\dfrac{E_2^*}{\boldsymbol{R}T_\mathrm{b}}\right)$