Problem 1-13 Half-life, activation energy

Thermal decomposition of a hydrocarbon is a second-order reaction. At the temperature of 500 °C the value of the half-life was found to be 8.7 min and at 548 °C one half of the same initial hydrocarbon amount was decomposed in 3.9 min. Calculate the activation energy of the decomposition reaction.

[$E^* = 88.230$ kJ mol^{-1}]

Solution:

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{E^*}{\boldsymbol{R}T^2}$$

$$E^* = \frac{\boldsymbol{R}\cdot\ln(k_2/k_1)}{\frac{1}{T_1}-\frac{1}{T_2}}$$

$T_1 = 773.15$ K $\qquad (\tau_{1/2})_1 = 8.7$ min

$T_2 = 821.15$ K $\qquad (\tau_{1/2})_2 = 3.9$ min

$(c_{A0})_1 = (c_{A0})_2 = c_{A0}$

Second order: $\tau_{1/2}\cdot k_c = \frac{1}{c_A}-\frac{1}{c_{A0}} = \frac{1}{0.5\,c_{A0}}-\frac{1}{c_{A0}} = \frac{1}{c_{A0}}$

$$k_{c1} = \frac{1}{(\tau_{1/2})_1\cdot c_{A0}} \quad , \quad k_{c2} = \frac{1}{(\tau_{1/2})_2\cdot c_{A0}}$$

$$\frac{k_{c2}}{k_{c1}} = \frac{(\tau_{1/2})_1}{(\tau_{1/2})_2}$$

$$E^* = \frac{\boldsymbol{R}\cdot\ln\frac{(\tau_{1/2})_1}{(\tau_{1/2})_2}}{\frac{1}{T_1}-\frac{1}{T_2}} = \frac{8.314\cdot\ln\frac{8.7}{3.9}}{\frac{1}{773.15}-\frac{1}{821.15}}$$

$E^* = 88\,230$ J mol^{-1}