Problem 1-12 First-order reaction [*V*], temperature dependence

The rate constant of the unidirectional decomposition A = R + 2 S at the temperature of 400 K is $5 \cdot 10^{-4}$ min^{-1}. The activation energy of this reaction has the value of 50 kJ mol^{-1}. Determine

(a) what is the percentage of A decomposed at 400 K in 50 minutes from the beginning of the reaction,

(b) to which temperature should be warmed the system in order that ten times greater amount of A than at 400 K was decomposed during the same time interval

[(a) 2.47 % A is decomposed; (b) T_2 = 477.1 K ($k_{c2} = 5.6738 \cdot 10^{-3}$ min^{-1})]

Solution:

(a) $T_1 = 400$ K , $k_1 = 5 \cdot 10^{-4}$ min^{-1}

$\tau = 50$ min , degree of conversion α = ?

$$\alpha = \frac{c_{A0} - c_A}{c_{A0}} \quad \Rightarrow \quad c_A = c_{A0} - c_{A0} \cdot \alpha$$

$$k_c \cdot \tau = \ln \frac{c_{A0}}{c_A} = \ln \frac{c_{A0}}{c_{A0} - c_{A0} \cdot \alpha} = -\ln (1 - \alpha)$$

$\ln (1 - \alpha_1) = -5 \cdot 10^{-4} \cdot 50 = -0.025$

$(1 - \alpha_1) = 0.9753$

$\alpha_1 = 0.0247$ .... 2.47 % A is decomposed

(b) $E = 50$ kJ mol^{-1} = 50 000 J mol^{-1}

T_2 = ?

in $\tau = 50$ min should be decomposed $\alpha_2 = 10\ \alpha_1 = 10 \cdot 0.0247 = 0.247$

$$k_{c2} = -\frac{1}{\tau} \ln (1 - \alpha_2) = -\frac{1}{50} \cdot \ln (1 - 0.247)$$

$k_{c2} = 5.6738 \cdot 10^{-3}$ min^{-1}

$$E \cdot \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \boldsymbol{R} \cdot \ln \frac{k_{c2}}{k_{c1}}$$

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{\boldsymbol{R}}{E} \cdot \ln \frac{k_{c2}}{k_{c1}} = \frac{1}{400} - \frac{8.314}{50000} \cdot \ln \frac{5.6738 \cdot 10^{-3}}{5 \cdot 10^{-4}} = 2.0961 \cdot 10^{-3}$$

$T_2 = 477.075$ K