Problem 2-05 Reversible first-order reactions, calculation of rate and equilibrium constants

Izomeration of *cis*-1,2-dimethylcyclopropane to *trans*-1,2-dimethylcyclopropane at the temperature of 450 °C follow the first order kinetics in both directions. Use experimental data given in the following table to calculate the equilibrium constant and the rate constant of the forward and backward reaction.

τ (s)	0	225	equilibrium
cis-form (%)	100	62.3	32.0

[K_c = 2.125 ; k_{c1} = 2.443·10^{-3} s^{-1} ; k_{c2} = 1.15·10^{-3} s^{-1}]

Solution:

Balance: (C stands for *cis*-isomer, T for *trans*-isomer)

$c_C = c_{C0} - x = 100 - x$

$c_T = x$

$\Sigma c = 100$

$\tau = 0$ $\quad c_{C0} = 100$, $\quad c_{T0} = 0$

$\tau = 225$ s $\quad c_C = 62.3$, $\quad c_T = x = 100 - 62.3 = 37.7$

$\tau \to \infty$ $\quad c_{C,equil} = 32$, $\quad c_{T,equil} = 68$

$$K_c = \frac{c_{T,\,equil}}{c_{C,\,equil}} = \frac{68}{32} = 2.125$$

$$-\frac{dc_C}{d\tau} = k_{c1} \cdot c_C - k_{c2} \cdot c_T$$

$$\frac{dx}{d\tau} = k_{c1} \cdot (c_{C0} - x) - k_{c2} \cdot x = k_{c1} \cdot (c_{C0} - x \cdot \frac{K_c + 1}{K_c})$$

$$-\ln \frac{c_{A0} - x \cdot (\frac{K_c + 1}{K_c})}{c_{A0}} = k_{c1} \cdot \frac{K_c + 1}{K_c} \cdot \tau$$

$$k_{c1} = -\frac{K_c}{(K_c + 1) \cdot \tau} \cdot \ln\left(1 - \frac{x}{c_{A0}} \cdot (\frac{K_c + 1}{K_c})\right) = -\frac{2.125}{(2.125 + 1) \cdot 225} \cdot \ln\left(1 - \frac{37.7}{100} \cdot \frac{2.125 + 1}{2.125}\right)$$

$k_{c1} = 2.443 \cdot 10^{-3}$ s^{-1}

$$k_{c2} = \frac{k_{c1}}{K_c} = \frac{2.443 \cdot 10^{-3}}{2.125} = 1.15 \cdot 10^{-3} \text{ s}^{-1}$$