Problem 3-04 Reaction mechanism

The following mechanism was proposed for the reaction **N_2O_5 (g) + NO (g) = 3 NO_2** (g):

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_2} N_2O_5$$

$$NO + NO_3 \xrightarrow{k_3} 2\ NO_2$$

Experiments revealed that the rate of N_2O_5 extinction is independent of NO concentration. Under which circumstances will the proposed mechanism correspond to experimentally found fact that the reaction follows the first-order kinetics?

$$\left[-\frac{\mathrm{d}c_{N_2O_5}}{\mathrm{d}\tau} = \frac{k_3 \cdot k_1 \cdot c_{N_2O_5} \cdot c_{NO}}{k_2 \cdot c_{NO_2} + k_3 \cdot c_{NO}},\ \text{for}\ k_2 \cdot c_{NO_2} << k_3 \cdot c_{NO} :\ -\frac{\mathrm{d}c_{N_2O_5}}{\mathrm{d}\tau} = k_1 \cdot c_{N_2O_5}\right]$$

Solution:

The total reaction rate can be expressed as the rate of N_2O_5 decrease:

$$-\frac{\mathrm{d}c_{N_2O_5}}{\mathrm{d}\tau} = k_1 \cdot c_{N_2O_5} - k_2 \cdot c_{NO_2} \cdot c_{NO_3}$$

NO_3 is an unstable intermediate:

$$\frac{\mathrm{d}c_{NO_3}}{\mathrm{d}\tau} = 0 = k_1 \cdot c_{N_2O_5} - k_2 \cdot c_{NO_2} \cdot c_{NO_3} - k_3 \cdot c_{NO} \cdot c_{NO_3} \qquad \Rightarrow \qquad c_{NO_3} = \frac{k_1 \cdot c_{N_2O_5}}{k_2 \cdot c_{NO_2} + k_3 \cdot c_{NO}}$$

$$-\frac{\mathrm{d}c_{N_2O_5}}{\mathrm{d}\tau} = k_1 \cdot c_{N_2O_5} - k_2 \cdot c_{NO_2} \cdot \frac{k_1 \cdot c_{N_2O_5}}{k_2 \cdot c_{NO_2} + k_3 \cdot c_{NO}} =$$

$$= \frac{k_1 \cdot c_{N_2O_5} \cdot (k_2 \cdot c_{NO_2} + k_3 \cdot c_{NO})}{k_2 \cdot c_{NO_2} + k_3 \cdot c_{NO}} - \frac{k_2 \cdot c_{NO_2} \cdot k_1 \cdot c_{N_2O_5}}{k_2 \cdot c_{NO_2} + k_3 \cdot c_{NO}}$$

$$-\frac{\mathrm{d}c_{N_2O_5}}{\mathrm{d}\tau} = \frac{k_3 \cdot k_1 \cdot c_{N_2O_5} \cdot c_{NO}}{k_2 \cdot c_{NO_2} + k_3 \cdot c_{NO}}$$

In case that the second reaction is much faster than the first one

i.e. if $k_2 \cdot c_{NO_2} << k_3 \cdot c_{NO} \qquad \Rightarrow \qquad k_2 \cdot c_{NO_2} + k_3 \cdot c_{NO} \approx k_3 \cdot c_{NO}$,

we can write

$$-\frac{\mathrm{d}c_{N_2O_5}}{\mathrm{d}\tau} = \frac{\cancel{k_3 \cdot c_{NO}} \cdot k_1 \cdot c_{N_2O_5}}{\cancel{k_3 \cdot c_{NO}}} = k_1 \cdot c_{N_2O_5}$$