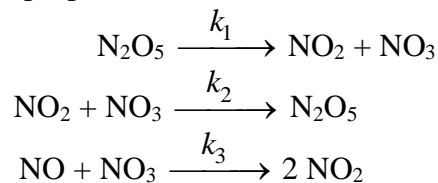


### Problem 3-04 Reaction mechanism

The following mechanism was proposed for the reaction  $\text{N}_2\text{O}_5 (\text{g}) + \text{NO} (\text{g}) = 3 \text{NO}_2 (\text{g})$ :



Experiments revealed that the rate of  $\text{N}_2\text{O}_5$  extinction is independent of  $\text{NO}$  concentration. Under which circumstances will the proposed mechanism correspond to experimentally found fact that the reaction follows the first-order kinetics?

$$\left[ -\frac{dc_{\text{N}_2\text{O}_5}}{d\tau} = \frac{k_3 \cdot k_1 \cdot c_{\text{N}_2\text{O}_5} \cdot c_{\text{NO}}}{k_2 \cdot c_{\text{NO}_2} + k_3 \cdot c_{\text{NO}}}, \text{ for } k_2 \cdot c_{\text{NO}_2} \ll k_3 \cdot c_{\text{NO}} : -\frac{dc_{\text{N}_2\text{O}_5}}{d\tau} = k_1 \cdot c_{\text{N}_2\text{O}_5} \right]$$

**Solution:**

The total reaction rate can be expressed as the rate of  $\text{N}_2\text{O}_5$  decrease:

$$-\frac{dc_{\text{N}_2\text{O}_5}}{d\tau} = k_1 \cdot c_{\text{N}_2\text{O}_5} - k_2 \cdot c_{\text{NO}_2} \cdot c_{\text{NO}_3}$$

$\text{NO}_3$  is an unstable intermediate:

$$\frac{dc_{\text{NO}_3}}{d\tau} = 0 = k_1 \cdot c_{\text{N}_2\text{O}_5} - k_2 \cdot c_{\text{NO}_2} \cdot c_{\text{NO}_3} - k_3 \cdot c_{\text{NO}} \cdot c_{\text{NO}_3} \quad \Rightarrow \quad c_{\text{NO}_3} = \frac{k_1 \cdot c_{\text{N}_2\text{O}_5}}{k_2 \cdot c_{\text{NO}_2} + k_3 \cdot c_{\text{NO}}}$$

$$\begin{aligned}-\frac{dc_{\text{N}_2\text{O}_5}}{d\tau} &= k_1 \cdot c_{\text{N}_2\text{O}_5} - k_2 \cdot c_{\text{NO}_2} \cdot \frac{k_1 \cdot c_{\text{N}_2\text{O}_5}}{k_2 \cdot c_{\text{NO}_2} + k_3 \cdot c_{\text{NO}}} = \\ &= \frac{k_1 \cdot c_{\text{N}_2\text{O}_5} \cdot (k_2 \cdot c_{\text{NO}_2} + k_3 \cdot c_{\text{NO}})}{k_2 \cdot c_{\text{NO}_2} + k_3 \cdot c_{\text{NO}}} - \frac{k_2 \cdot c_{\text{NO}_2} \cdot k_1 \cdot c_{\text{N}_2\text{O}_5}}{k_2 \cdot c_{\text{NO}_2} + k_3 \cdot c_{\text{NO}}} \\ -\frac{dc_{\text{N}_2\text{O}_5}}{d\tau} &= \frac{k_3 \cdot k_1 \cdot c_{\text{N}_2\text{O}_5} \cdot c_{\text{NO}}}{k_2 \cdot c_{\text{NO}_2} + k_3 \cdot c_{\text{NO}}}\end{aligned}$$

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

i.e. if  $k_2 \cdot c_{\text{NO}_2} \ll k_3 \cdot c_{\text{NO}} \quad \Rightarrow \quad k_2 \cdot c_{\text{NO}_2} + k_3 \cdot c_{\text{NO}} \approx k_3 \cdot c_{\text{NO}}$ ,  
we can write

$$-\frac{dc_{\text{N}_2\text{O}_5}}{d\tau} = \frac{\cancel{k_3 \cdot c_{\text{NO}}} \cdot k_1 \cdot c_{\text{N}_2\text{O}_5}}{\cancel{k_3 \cdot c_{\text{NO}}}} = k_1 \cdot c_{\text{N}_2\text{O}_5}$$