# Chapter 11 – Problems 78, 80

Michael Brodskiy

Instructor: Mr. Morgan

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78. For the following reaction, the experimental rate expression is rate $= k[\mathrm{NO}]^2[\mathrm{H_2}]$. The following mechanism is proposed. Is this mechanism consistent with the rate expression?

$$2\,\mathrm{H_2(g)} + 2\,\mathrm{NO\,(g)} \longrightarrow \mathrm{N_2(g)} + 2\,\mathrm{H_2O\,(g)}$$

$$\begin{aligned} 2\,\mathrm{NO} &\rightleftharpoons \mathrm{N_2O_2} && \text{(fast)} \\ \mathrm{N_2O_2} + \mathrm{H_2} &\longrightarrow \mathrm{H_2O} + \mathrm{N_2O} && \text{(slow)} \\ \mathrm{N_2O} + \mathrm{H_2} &\longrightarrow \mathrm{N_2} + \mathrm{H_2O} && \text{(fast)} \end{aligned} \tag{1}$$

Yes, it is consistent, because $\mathrm{N_2O_2}$ may be substituted for $2\,\mathrm{NO}$, which, in turn, can be changed into $[\mathrm{NO}]^2$.

80. Two mechanisms are proposed for the following reaction. Show that each of these mechanisms is consistent with the observed rate law: rate $= k[\mathrm{NO}]^2[\mathrm{O_2}]$

$$2\,\mathrm{NO\,(g)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{NO_2(g)}$$

$$\begin{aligned} \text{Mechanism 1:} \quad \mathrm{NO} + \mathrm{O_2} &\rightleftharpoons \mathrm{NO_3} && \text{(fast)} \\ \mathrm{NO_3} + \mathrm{NO} &\longrightarrow 2\,\mathrm{NO_2} && \text{(slow)} \\ \text{Mechanism 2:} \quad \mathrm{NO} + \mathrm{NO} &\rightleftharpoons \mathrm{N_2O_2} && \text{(fast)} \\ \mathrm{N_2O_2} + \mathrm{O_2} &\longrightarrow 2\,\mathrm{NO_2} && \text{(slow)} \end{aligned} \tag{2}$$

$$\begin{aligned} \mathrm{NO_3} &= \mathrm{NO} + \mathrm{O_2} \\ \mathrm{NO_3} + \mathrm{NO} &= 2\,\mathrm{NO_2} \\ \mathrm{O_2} + 2\,\mathrm{NO} &= 2\,\mathrm{NO_2} \\ \therefore &\text{ it is consistent} \end{aligned} \tag{3}$$

$$\begin{aligned} \mathrm{N_2O_2} &= 2\,\mathrm{NO} \\ \mathrm{N_2O_2} + \mathrm{O_2} &= 2\,\mathrm{NO_2} \\ 2\,\mathrm{NO} + \mathrm{O_2} &= 2\,\mathrm{NO_2} \\ \therefore &\text{ it is consistent} \end{aligned} \tag{4}$$