ChE-403 Problem Set 1.4

Week 4

Problem 1

Consider the decomposition of N_2O_5:

$$2N_2O_5 \Rightarrow 4NO_2 + O_2$$

Experimentally, we observe that the rate of oxygen formation is consistent with the following expression:

$$\frac{d[O_2]}{dt} = k[N_2O_5]$$

With k being a constant.

Is this compatible with the following suggested mechanism?

$$2(N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3)$$

$$NO_2 + NO_3 \xrightarrow{k_2} NO_2 + O_2 + NO$$

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

$$2N_2O_5 \Rightarrow 4NO_2 + O_2$$

Solution:

$$\frac{d[O_2]}{dt} = k_2[NO_2][NO_3]$$

From reaction we have an equilibrium:

$$k_1[N_2O_5] = k_{-1}[NO_2][NO_3]$$

$$\to K = \frac{k_1}{k_{-1}} = \frac{[NO_2][NO_3]}{[N_2O_5]} \to [NO_2][NO_3] = K[N_2O_5]$$

$$\to \frac{d[O_2]}{dt} = k_2K[N_2O_5] = k[N_2O_5]$$

With: $k = k_2K$

So, Yes! This mechanism is compatible with the mathematical expression given above.

Problem 2
Consider the decomposition of ozone catalyzed by *Cl*:

$$Cl + O_3 \xrightarrow{k_1} O_2 + ClO$$

$$\frac{ClO + O \xrightarrow{k_2} O_2 + Cl}{O + O_3 \Rightarrow 2O_2}$$

Can you use the steady state approximation on reactive intermediate *ClO* to show that the rate of ozone disappearance can be written as:

$$\frac{d[O_3]}{dt} = -\frac{k_1 k_2 [O][O_3][Cl]_0}{k_2[O] + k_1[O_3]}$$

Where $[Cl]_0$ is the Cl loaded/present in the system at t=0.

Solution:

The steady state approximation allows us to set the rate of change of reactive intermediates during the reaction to zero. Let's do that for *ClO*:

$$\frac{d[ClO]}{dt} = 0 = k_1[Cl][O_3] - k_2[ClO][O] \quad *$$

$$[ClO] = \frac{k_1[Cl][O_3]}{k_2[O]}$$

Let's do a balance on Cl: $[Cl]_0 = [Cl] + [ClO]$

And substitute $[Cl]$:

$$[ClO] = \frac{k_1[O_3]}{k_2[O]}([Cl]_0 - [ClO])$$

$$[ClO]\left(1 + \frac{k_1[O_3]}{k_2[O]}\right) = \frac{k_1[O_3]}{k_2[O]}[Cl]_0$$

$$[ClO] = \frac{k_1[O_3][Cl]_0}{k_2[O] + k_1[O_3]}$$

The rate of ozone decomposition is:

$$\frac{d[O_3]}{dt} = -k_1[Cl][O_3]$$

But from * we know that $k_1[Cl][O_3] = k_2[ClO][O]$

Side note:

This equality perfectly illustrates that with the SSA, we have:

$$\frac{d\Phi(t)}{dt} = \frac{1}{\nu_1}\frac{d\mathrm{n}_1}{dt} = \cdots = \frac{1}{\nu_i}\frac{d\mathrm{n}_\mathrm{i}}{dt}$$

Therefore we can write:

$$\frac{d[O_3]}{dt} = -\frac{k_1 k_2[O][O_3][Cl]_0}{k_2[O] + k_1[O_3]}$$