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?

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

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

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

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

Solution:

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

From reaction we have an equilibrium:

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

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

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

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

Problem 3
The formation of HBr from H_2 and Br_2 occurs through the following steps:

$$Br + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HBr + H$$

$$H + Br_2 \xrightarrow{k_2} HBr + Br$$

$$Br_2 \overset{K_3}{\rightleftharpoons} 2Br$$

Can you derive a rate expression that looks like the following?

$$\frac{d[H_2]}{dt} = -\frac{cst1\ [Br_2]^{1/2}[H_2]}{1 + cst2\ \left(\frac{[HBr]}{[Br_2]}\right)}$$

What are the expressions of cst1 and cst2?

Solution:

$$Br + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HBr + H \qquad (1)$$

$$H + Br_2 \overset{k_2}{\rightarrow} HBr + Br \qquad (2)$$

$$Br_2 \overset{K_3}{\rightleftharpoons} 2Br \qquad (3)$$

Since reaction (3) is at equilibrium, we have…

$$\frac{d[Br_2]}{dt} = k_{-3}[Br]^2 - k_3[Br_2] = 0 \quad \rightarrow \quad K_3 = \frac{[Br]^2}{[Br_2]} \quad or \quad [Br] = [Br_2]^{\frac{1}{2}}\, K_3{}^{\frac{1}{2}}$$

We write the expression of the change in concentration of hydrogen with time...

$$\frac{d[H]}{dt} = k_1[Br][H_2] - k_{-1}[HBr][H] - k_2[H][Br_2]$$

We can assume that this rate is at steady state, because it concerns H radicals. We can apply the SSA ($\frac{d[H]}{dt} = 0$) and determine [H]

$$[H] = \frac{k_1[Br][H_2]}{k_{-1}[HBr] + k_2[\,Br_2]}$$

We write the expression of the change in concentration of dihydrogen with time and substitute [H] and [Br]…

$$\frac{d[H_2]}{dt} = k_{-1}[HBr][H] - k_1[H_2][Br]$$

$$\frac{d[H_2]}{dt} = k_{-1}[HBr]\left(\frac{k_1\left([Br_2]^{\frac{1}{2}}\,K_3{}^{\frac{1}{2}}\right)[H_2]}{k_{-1}[HBr] + k_2[\,Br_2]}\right) - k_1[H_2]\left([Br_2]^{\frac{1}{2}}\,K_3{}^{\frac{1}{2}}\right)$$

$$\frac{d[H_2]}{dt} = k_1[H_2]\left([Br_2]^{\frac{1}{2}}\,K_3{}^{\frac{1}{2}}\right)\left[\frac{k_{-1}[HBr]}{k_{-1}[HBr] + k_2[\,Br_2]} - 1\right]$$

$$= k_1[H_2]\left([Br_2]^{\frac{1}{2}}\,K_3{}^{\frac{1}{2}}\right)\left[\frac{k_{-1}[HBr] - k_{-1}[HBr] - k_2[\,Br_2]}{k_{-1}[HBr] + k_2[\,Br_2]}\right]$$

$$= k_1[H_2]\left([Br_2]^{\frac{1}{2}}\,K_3{}^{\frac{1}{2}}\right)\left[\frac{-k_2[\,Br_2]}{k_{-1}[HBr] + k_2[\,Br_2]}\right]$$

We simplify…

$$\frac{d[H_2]}{dt} = -\frac{k_1\,K_3{}^{\frac{1}{2}}[Br_2]^{\frac{1}{2}}[H_2]}{1 + \frac{k_{-1}[HBr]}{k_2[\,Br_2]}}$$

Therefore…

$$cst1 = k_1\,K_3{}^{\frac{1}{2}} \quad and \quad cst2 = \frac{k_{-1}}{k_2}$$