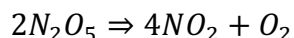


ChE-403 Problem Set 1.4

Week 4

Problem 1

Consider the decomposition of N_2O_5 :

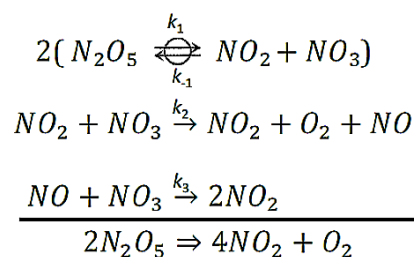


Experimentally, we observe that the rate of oxygen formation is consistent with the following expression:

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

With k being a constant.

Is this compatible with the following suggested mechanism?



Solution:

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

From reaction we have an equilibrium:

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

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

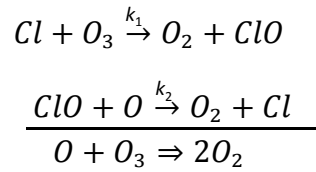
$$\rightarrow \frac{d[O_2]}{dt} = k_2K[N_2O_5] = k[N_2O_5]$$

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 :



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:

$$\frac{d\Phi(t)}{dt} = \frac{1}{\nu_1} \frac{dn_1}{dt} = \dots = \frac{1}{\nu_i} \frac{dn_i}{dt}$$

Therefore we can write:

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