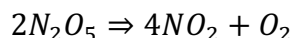


ChE-403 Problem Set 1.4

Week 4

Problem 1

Consider the decomposition of N_2O_5 :

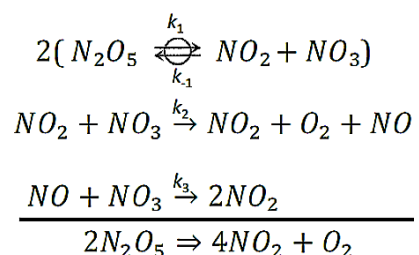


Experimentally, we observe that the rate of oxygen formation is consistent with the following expression:

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

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:

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

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

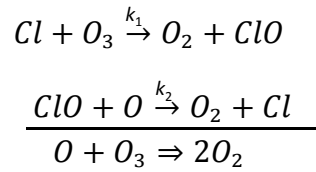
$$\rightarrow \frac{d[O_2]}{dt} = k_2K[N_2O_5] = k[N_2O_5]$$

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:

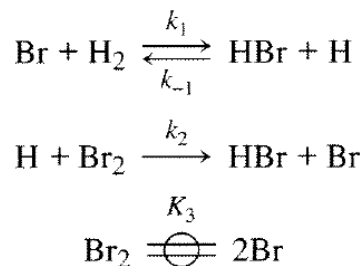
$$\frac{d\Phi(t)}{dt} = \frac{1}{\nu_1} \frac{dn_1}{dt} = \dots = \frac{1}{\nu_i} \frac{dn_i}{dt}$$

Therefore we can write:

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

Problem 3

The formation of HBr from H₂ and Br₂ occurs through the following steps:

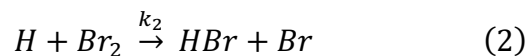
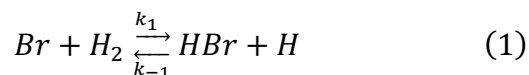


Can you derive a rate expression that looks like the following?

$$\frac{d[\text{H}_2]}{dt} = -\frac{cst1 [\text{Br}_2]^{1/2} [\text{H}_2]}{1 + cst2 \left(\frac{[\text{HBr}]}{[\text{Br}_2]} \right)}$$

What are the expressions of cst1 and cst2?

Solution:



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

$$\frac{d[\text{Br}_2]}{dt} = k_{-3}[\text{Br}]^2 - k_3[\text{Br}_2] = 0 \quad \rightarrow \quad K_3 = \frac{[\text{Br}]^2}{[\text{Br}_2]} \quad \text{or} \quad [\text{Br}] = [\text{Br}_2]^{\frac{1}{2}} K_3^{\frac{1}{2}}$$

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

$$\frac{d[\text{H}]}{dt} = k_1[\text{Br}][\text{H}_2] - k_{-1}[\text{HBr}][\text{H}] - k_2[\text{H}][\text{Br}_2]$$

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

$$[\text{H}] = \frac{k_1[\text{Br}][\text{H}_2]}{k_{-1}[\text{HBr}] + k_2[\text{Br}_2]}$$

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

$$\begin{aligned}\frac{d[H_2]}{dt} &= k_{-1}[HBr][H] - k_1[H_2][Br] \\ \frac{d[H_2]}{dt} &= k_{-1}[HBr] \left(\frac{k_1 \left([Br_2]^{\frac{1}{2}} K_3^{\frac{1}{2}} \right) [H_2]}{k_{-1}[HBr] + k_2[Br_2]} \right) - k_1[H_2] \left([Br_2]^{\frac{1}{2}} K_3^{\frac{1}{2}} \right) \\ \frac{d[H_2]}{dt} &= k_1[H_2] \left([Br_2]^{\frac{1}{2}} K_3^{\frac{1}{2}} \right) \left[\frac{k_{-1}[HBr]}{k_{-1}[HBr] + k_2[Br_2]} - 1 \right] \\ &= k_1[H_2] \left([Br_2]^{\frac{1}{2}} K_3^{\frac{1}{2}} \right) \left[\frac{k_{-1}[HBr] - k_{-1}[HBr] - k_2[Br_2]}{k_{-1}[HBr] + k_2[Br_2]} \right] \\ &= k_1[H_2] \left([Br_2]^{\frac{1}{2}} K_3^{\frac{1}{2}} \right) \left[\frac{-k_2[Br_2]}{k_{-1}[HBr] + k_2[Br_2]} \right]\end{aligned}$$

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...

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