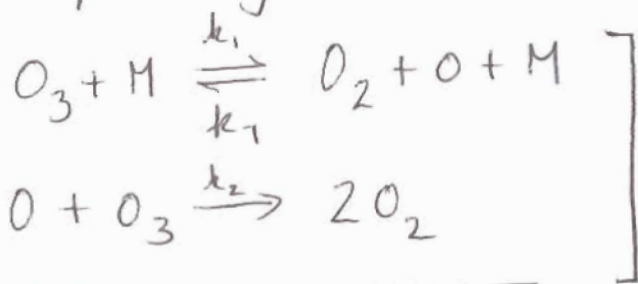


Steady State Approximation

W

P

Chapman Cycle for Ozone Decomposition



M is an inert collision partner

asked about the condition of $[\text{O}_2] = 0$ is it undefined? No, this rate law is developed from the following analysis where $[\text{O}_2]$ is greater than $[\text{O}_3]$



• What species is the intermediate? O

• RDS is unknown, i.e. no assumptions are made about the relative rates.

$$\therefore -\frac{d[\text{O}_3]}{dt} = \underset{\text{positive rate}}{k_1 [\text{O}_3][\text{M}]} - \underset{\text{negative rate}}{k_{-1} [\text{O}_2][\text{O}][\text{M}]} + \underset{\text{positive rate}}{k_2 [\text{O}][\text{O}_3]}$$

An assumption we can make is that $\frac{d[\text{O}]}{dt} \approx 0$
i.e. the intermediate is used up as fast as it is made.

$\frac{d[\text{O}]}{dt}$ is determined by one productive rxn and two destructive rxns.

$$\text{Algebraically this is: } \frac{d[\text{O}]}{dt} \approx 0 = k_1 [\text{O}_3][\text{M}] - k_{-1} [\text{O}_2][\text{O}][\text{M}] - k_2 [\text{O}][\text{O}_3]$$

$$\text{Solve for } [\text{O}] = \frac{k_1 [\text{O}_3][\text{M}]}{k_{-1} [\text{O}_2][\text{M}] + k_2 [\text{O}_3]} \quad \rightarrow \text{rate of formation}$$

• How to use this solution, simplistically:

Write the rate law in terms of a reactant and intermediate, i.e.

rate = $k_2 [\text{O}][\text{O}_3]$, and substitute the expression for $[\text{O}]$

So...
$$\text{rate} = \frac{k_2 k_1 [O_3]^2 [H]}{k_{-1} [O_2] [H] + k_2 [O_3]}$$

Then consider extremes: if $[O_3]$ is high, then $\text{rate} = k_1 [O_3] [H]$

if $[O_2]$ is high, then $\text{rate} = \frac{k_2 k_1 [O_3]^2}{k_{-1} [O_2]}$

(alternatively, if $k_1 [O_3] [H] \ll k_{-1} [O_2] [O] [H]$ ($k_2 [O_3] [O]$),
 i.e. $k_1 [O_3] [H]$ is RDS, then $\text{rate} = \frac{k_2 k_1 [O_3]^2 [H]}{k_{-1} [O_2] [H] + k_2 [O_3]}$
 if $k_{-1} [O_2] [H] \ll k_1 [O_3] [H]$ ($k_2 [O_3] [O]$)
 i.e. $k_{-1} [O_2] [H]$ is RDS, then $\text{rate} = k_1 [O_3] [H]$)

More Complex Solution: $\text{rate} = -\frac{d[O_3]}{dt} = k_1 [O_3] [H] - k_{-1} [O_2] [O] [H] + k_2 [O_3] [O]$
 substitute $[O] = \frac{k_1 [O_3] [H]}{k_{-1} [O_2] [H] + k_2 [O_3]}$

$$\text{rate} = k_1 [O_3] [H] - \frac{k_{-1} [O_2] k_1 [O_3] [H]^2}{k_{-1} [O_2] [H] + k_2 [O_3]} + \frac{k_2 [O_3]^2 k_1 [H]}{k_{-1} [O_2] [H] + k_2 [O_3]}$$

$$\text{rate} = \frac{k_1 k_1 [O_3] [O_2] [H]^2}{k_{-1} [O_2] [H] + k_2 [O_3]} + \frac{k_2 [O_3]^2 [H] k_1}{k_{-1} [O_2] [H] + k_2 [O_3]} - \frac{k_{-1} [O_2] k_1 [O_3] [H]^2}{k_{-1} [O_2] [H] + k_2 [O_3]} + \frac{k_2 [O_3]^2 k_1 [H]}{k_{-1} [O_2] [H] + k_2 [O_3]}$$

call $k_{-1} [O_2] [H] + k_2 [O_3] = X$

$$\text{rate} = \frac{k_{-1} k_1 [O_3] [O_2] [H]^2}{X} + \frac{k_2 [O_3]^2 [H] k_1}{X} - \frac{k_{-1} [O_2] k_1 [O_3] [H]^2}{X} + \frac{k_2 [O_3]^2 k_1 [H]}{X}$$

$$\text{rate} = \frac{2 k_1 k_2 [O_3]^2 [H]}{X} = \frac{2 k_1 k_2 [O_3]^2 [H]}{k_{-1} [O_2] [H] + k_2 [O_3]}$$