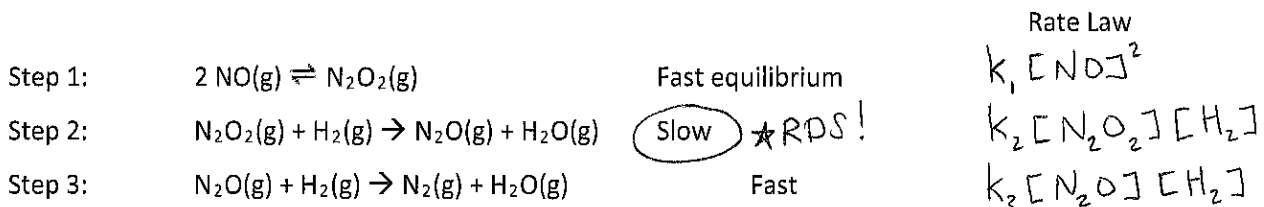


Mechanisms with a Fast Initial Step

1. When a mechanism contains a fast initial step, the rate limiting step may contain intermediates.
2. When a previous step is rapid and reaches equilibrium, the forward and reverse reaction rates are equal, so the concentrations of reactants and products of the the step are related, and the product is an intermediate.
3. Substituting into the rate law of RDS will produce a rate law in terms of just reactants.

Example: Nitrogen oxide is reduced to hydrogen gas to give water and nitrogen: $2 \text{H}_2(\text{g}) + 2 \text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$
The experimentally determined rate law for this reaction is: $\text{rate} = k[\text{H}_2][\text{NO}]^2$

One possible mechanism to account for this reaction is:



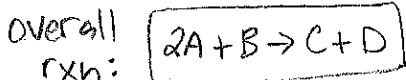
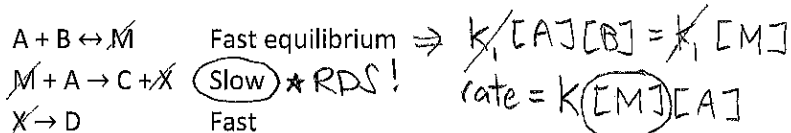
To determine the rate law,

1. Write the rate law for the slow step: $\text{rate} = k [\text{N}_2\text{O}_2][\text{H}_2]$ (intermediate!)
2. Substitute reactants from the equilibrium step to replace any intermediates in the rate law: *replace w/*
*@equilibrium, $\text{rate}_{\text{forward}} = \text{rate}_{\text{backwards}}$

$$K_{\text{eq}} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \Rightarrow [\text{N}_2\text{O}_2] = K_{\text{eq}} [\text{NO}]^2$$

Let's Practice! $\text{rate} = k (K_{\text{eq}} [\text{NO}]^2) [\text{H}_2] = k [\text{NO}]^2 [\text{H}_2]$

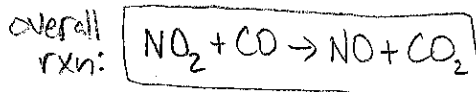
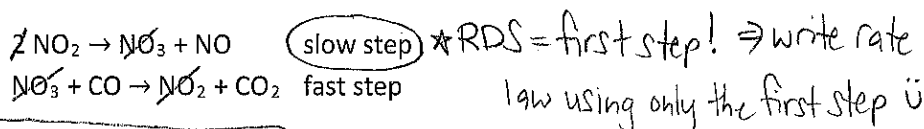
1. Write the rate law for the mechanism shown below. What is the overall reaction?



$$\text{rate} = k [\text{A}]^2 [\text{B}]$$

↳ intermediate → replace using fast equil step!

2. Write the rate law for the mechanism shown below. What is the overall reaction?



$$\text{rate} = k [\text{NO}_2]^2$$