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: $2\ H_2(g) + 2\ NO(g) \rightarrow N_2(g) + 2\ H_2O(g)$

The experimentally determined rate law for this reaction is: rate = $k[H_2][NO]^2$

One possible mechanism to account for this reaction is:

			Rate Law
Step 1:	$2\ NO(g) \rightleftharpoons N_2O_2(g)$	Fast equilibrium	$k_1[NO]^2$
Step 2:	$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$	Slow ★RDS!	$k_2[N_2O_2][H_2]$
Step 3:	$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$	Fast	$k_3[N_2O][H_2]$

To determine the rate law,

1. Write the rate law for the slow step: rate $= k[N_2O_2][H_2]$ ← intermediate!
2. Substitute reactants from the equilibrium step to replace any intermediates in the rate law: replace w/

★@ equilibrium, $rate_{forward} = rate_{backwards}$

$$K_{eq} = \frac{[N_2O_2]}{[NO]^2} \Rightarrow [N_2O_2] = K_{eq}[NO]^2$$

rate $= k(K_{eq}[NO]^2)[H_2] = k[NO]^2[H_2]$

Let's Practice!

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

$A + B \leftrightarrow M$ Fast equilibrium ⇒ $k_1[A][B] = k_{-1}[M]$

$M + A \rightarrow C + X$ Slow ★RDS! rate $= k[M][A]$

$X \rightarrow D$ Fast

↳ intermediate → replace using fast equil step!

overall rxn: $2A + B \rightarrow C + D$

rate $= k[A]^2[B]$

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

$2\ NO_2 \rightarrow NO_3 + NO$ slow step ★RDS = first step! ⇒ write rate law using only the first step ü

$NO_3 + CO \rightarrow NO_2 + CO_2$ fast step

overall rxn: $NO_2 + CO \rightarrow NO + CO_2$

⇓

rate $= k[NO_2]^2$