Complicated Mechanism & Rate Law

Reaction: $2\,NO_2 + F_2 \rightarrow 2\,NO_2F$

Mechanism: ① $NO_2 + F_2 \rightarrow NO_2F + F$

② $F + NO_2 \rightarrow NO_2F$

If step ① is slowest, then:

$$\text{rate (overall)} = k[NO_2][F_2]$$ (easy)

If step ② is slowest, then:

$$\text{rate (overall)} = k_2[NO_2][F]$$

↑ cannot be part of overall rate, since it's an intermediate

So ....

We assume the fast step (1) is at equilibrium; meaning the forward & reverse of step ① are proceeding at the same rate:

Mathematically:

rate ① = rate ⑴

↑ reverse reaction

$$k_1[NO_2][F_2] = k_{-1}[NO_2F][F]$$

↘ rearrange

$$\frac{k_1[NO_2][F_2]}{k_{-1}[NO_2F]} = [F]$$

↖ substitute for [F] in overall rate

$$\text{rate (overall)} = \frac{k_2 k_1}{k_1} \frac{[NO_2][NO_2][F_2]}{[NO_2F]}$$

$$= k_{observed} \frac{[NO_2]^2[F_2]}{[NO_2F]}$$