Rate-Determining (Rate-Controlling) Steps

① $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X$ | $X \xrightarrow[\text{slow}]{k_1} A + B$

② $X \xrightarrow{k_2} Z$ | $X \xrightarrow[\text{fast}]{k_2} Z$

~~If we assume~~ The rate of formation of X from A + B (other steps are assumed to be absent) is

$$v_X = k_1 [A][B] \quad \text{——} (A)$$

Case I:

Assume $k_2 \gg k_{-1}$ that means that the intermediate is converted very rapidly into ~~X~~ Z, much more rapidly than it can go back into A + B.

Then the ~~the~~ formation of Z will be reduced into

$$v = v_Z = \frac{d[Z]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} [A][B]$$

comes from steady state approximation

$$= k_1 [A][B]$$

$$= v_X \longrightarrow (\text{from Eq. (A)})$$

Then the initial step ($A + B \xrightarrow{k_1} X$) is the rate determining step.

Case II

$$X \xrightarrow[\text{fast}]{k_1} A + B$$

$$X \xrightarrow[k_2]{\text{slow}} Z$$

$$k_2 \ll k_{-1}$$

① $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X$

② $X \xrightarrow{k_2} Z$

$$v = v_2 = \frac{d[Z]}{dt} = \frac{k_1 k_2}{k_{-1} + k_2}[A][B]$$

$$= \frac{k_1 k_2}{k_{-1}}[A][B]$$

Reaction ② $X \xrightarrow{k_2} Z$ is now the rate-determining step or the rate-controlling step.