

Reaction Mechanisms

Based on the idea that reactions follow a path of multiple steps, you need to be able to derive a rate expression from a reaction mechanism.

3 Basic Rules

1. The slow step is always rate determining.
2. For any step in the reaction mechanism you can just use its stoichiometric coefficient as its rate-order.
3. The final rate expression must include only species that are in the overall reaction. <-- use equilibrium expressions from fast steps to get rid of reaction intermediates.

For example:

The overall reaction is $2 \text{NO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons 2 \text{NOCl}_{(g)}$

The rate law is found to be second order in $\text{NO}_{(g)}$ and first order in $\text{Cl}_{2(g)}$. Derive this expression from the proposed reaction mechanism:

1. $\text{NO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons \text{NOCl}_{2(g)}$ fast
2. $\text{NOCl}_{2(g)} + \text{NO}_{(g)} \rightleftharpoons 2 \text{NOCl}_{(g)}$ slow

1. Slow step is rate determining: $r = k[\text{NOCl}_2][\text{NO}]$
2. NOCl_2 is a reaction intermediate so use an equilibrium constant expression to get rid of it.

$$K_C = \frac{[\text{NOCl}_2]}{[\text{NO}][\text{Cl}_2]} \quad [\text{NOCl}_2] = K_C[\text{NO}][\text{Cl}_2]$$

3. Plug in: $r = kK_C[\text{NO}][\text{Cl}_2][\text{NO}]$

$$r = kK_C[\text{NO}]^2[\text{Cl}_2]$$

So your final rate law is: $r = k'[\text{NO}]^2[\text{Cl}_2]$