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 NO(g) and first order in Cl$_2$(g). Derive this expression from the proposed reaction mechanism:

1. NO (g) + Cl$_2$(g) $\rightleftharpoons$ NOCl$_2$(g) fast
2. NOCl$_2$(s) + NO (g) $\rightleftharpoons$ 2 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: $r = k'[\text{NO}]^2[\text{Cl}_2]$