A First Course on Kinetics and Reaction Engineering

How To Generate a Rate Expression from a Mechanism

1. Determine whether there is a rate determining step
   a. If YES, follow a steps
   b. If NO, follow b steps
2.
   a. Set the overall rate expression equal to the rate expression for the rate determining step divided by its stoichiometric number, assuming it to be irreversible
   b. Pick a reactant or product of the overall reaction and set the rate expression for the overall rate of generation of that species equal to the sum of its rates of generation in each of the mechanistic steps
3. Simplify the resulting overall rate expression by eliminating terms corresponding to irreversible or kinetically insignificant steps
4. Decide whether the resulting rate expression is acceptable (it usually won't be because it will contain concentrations or partial pressures of reactive intermediates). If it is acceptable, you are done, if not, proceed to step 5
5.
   a. Write an equilibrium expression for every step except the rate determining step
   b. Apply the Bodenstein steady state approximation to every reactive intermediate
6. Simplify the equations resulting from step 6 by eliminating terms corresponding to irreversible or kinetically insignificant steps
7. If the mechanism involves a homogeneous catalyst or an enzyme, eliminate one of the equations from step 6 and replace it with the equation for conservation of catalyst
8. If the mechanism involves charged species, eliminate one of the equations from step 6 and replace it with the equation for conservation of charge
9. If the mechanism involves a heterogeneous catalyst, eliminate one of the equations from step 6 and replace it with the equation for conservation of catalytic sites
10. Solve the resulting set of equations to get expressions for each of the reactive intermediates in terms of constants (k's and K's), concentrations of stable species, and (if appropriate) the initial total amount of catalyst or enzyme
11. If there is a most abundant surface intermediate, further simplify the results of step 9 accordingly
12. Substitute the expressions for the concentrations of reactive intermediates (step 9 or step 10) into the rate expression (step 4)