

REACTION MECHANISMS

Many reaction mechanism problems will ask you to derive a rate law that is both :

1.) representative of the overall reaction (NOT simply the rate-determining step)

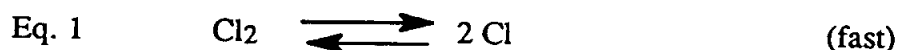
AND

2.) free of all intermediate species (those substances which do NOT appear in the overall rxn)

In order to accomplish this feat, you must use a combination of rate constant expressions and equilibrium constant expressions.

Use the following example as a general format in solving for the rate law of a reaction mechanism.

EX. Determine the rate law for the following reaction mechanism :



STEP 1 : Write a rate law for the slow step (rate-determining step) using reaction stoichiometry since all slow steps are elementary processes. This equation will serve as a sort of "skeleton" rate law which will be manipulated into one that satisfies our two opening conditions.

$$\text{rate} = k_2 [\text{Cl}][\text{CHCl}_3]$$

Dem. Rxns.

STEP 2: Compare the reactants in the slow step rate law with the reactants in the overall reaction.

You should notice that [Cl] is an intermediate, for it does not appear in the overall reaction. Hence, your goal is to delete [Cl] from the slow step rate law in order to create a NEW rate law that is representative of the OVERALL reaction.

STEP 3: Use a fast equation that contains both the intermediate and the reactant that are found in the overall reaction. Use this equation to write an equilibrium constant expression.

$$\text{From equation \#1} \quad K_1 = k_1/k_{-1} = [\text{Cl}\cdot]^2/[\text{Cl}_2]$$

STEP 4: Solve the equilibrium constant expression for the intermediate.

$$[\text{Cl}\cdot] = ((k_1/k_{-1}) [\text{Cl}_2])^{1/2} =$$

$$[\text{Cl}\cdot] = (k_1/k_{-1})^{1/2} ([\text{Cl}_2])^{1/2}$$

STEP 5: Substitute the value of $[\text{Cl}\cdot]$ determined in step 4 into the slow step rate law.

$$\text{For Equation 2, the slow step, rate 2} = k_2 [\text{Cl}\cdot] [\text{CHCl}_3]$$

$$= k_2 (k_1/k_{-1})^{1/2} ([\text{Cl}_2])^{1/2} [\text{CHCl}_3]$$

Let $k_2 (k_1/k_{-1})^{1/2} =$ a new constant called k , and substitute this k into the above equation to get the overall rate law.

$$\text{rate} = k ([\text{Cl}_2])^{1/2} [\text{CHCl}_3]$$

Now you have a rate law that satisfies both of the conditions outlined in the beginning of the handout.