# 5.111 Principles of Chemical Science

Fall 2008

## Reaction Mechanism

***See lectures 32 and 33 for determining reaction mechanisms.***

**Example from pg. 4 of Lecture 33 notes: The reaction mechanism of natural ozone depletion:**

Through a variety of catalytic cycles, Cl and Br ions catalyze the destruction of ozone in the stratosphere. However, at high concentrations, ozone decays into oxygen without metal catalysts required:

$2O_3 \rightarrow 3O_2$

proposed mechanism:

Step 1 (fast reversible): $O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ $\quad rate_f = k_1[O_3]$; $\quad rate_r = k_{-1}[O_2][O]$

Step 2 (slow): $O + O_3 \xrightarrow{k_2} O_2 + O_2$ $\quad rate = k_2[O][O_3]$

The rate is determined by the slowest step

The rate of formation of $O_2$ is equal to 2 times the rate of the slow step ($k_2[O][O_3]$), since two molecules of $O_2$ are formed.

Thus, rate of formation of $O_2 = 2k_2[O][O_3]$, but "O" is an intermediate, solve for "O" in terms of products and reactants and rate constants.

Since the first step is fast and reversible and the second step is slow, the first step is in equilibrium and we can write

$$\frac{[O_2][O]}{[O_3]} = \frac{k_1}{k_{-1}} = K_1 \qquad \text{or} \qquad [O] = \frac{k_1\,[O_3]}{k_{-1}\,[O_2]}$$

substituting:

$$\text{rate} = \frac{2k_2\,k_1\,[O_3]^2}{k_{-1}\,[O_2]}$$

$$\text{rate} = k_{obs}\,\frac{[O_3]^2}{[O_2]}$$

What is the order in $O_3$? *2*
What is the order in $O_2$? *-1*
What is the overall order? *1*

double $O_3$/rate will? *multiply by 4*
double $O_2$/ *multiply by ½*
double both $O_3$ and $O_2$/ *double*