Chemistry 146 Lecture Problems
Rate Law

With the rate equation written as: $Rate = k \cdot A^x \cdot B^y$

The rate may be measured experimentally for a given concentration of A and B. However, the rate constant (k) and the order of the reaction in A (x) and the order of the reaction in B (y) are still unkown. One method for determining the rate constant (k) is to preform the experiment under two sets of experimental conditions so that:

$$\frac{Rate_1}{Rate_2} = \frac{k \cdot (A_1)^x \cdot (B_1)^y}{k \cdot (A_2)^x \cdot (B_2)^y}$$

This experiment may be done two ways. By using a large excess of B, only A changes concentration. Or using initial rates for two different concentrations of A, with the same concentration of B. Since k and B are constant under these conditions:

$$\frac{Rate_1}{Rate_2} = \frac{{A_1}^x}{{A_2}^x}$$

$$\frac{Rate_1}{Rate_2} = \left(\frac{A_1}{A_2}\right)^x$$

$$\ln\left(\frac{Rate_1}{Rate_2}\right) = x \cdot \ln\left(\frac{A_1}{A_2}\right)$$

For the reaction:

NH4 + NO2- -> N2 + 2 H2O

With the following experimental data:

$[NH_4^{1+}]$ (M)	$[NO_2^{1-}]$ (M)	Rate (M sec^{-1})
0.100	0.0050	$1.35*10^{-7}$
0.100	0.010	$2.75*10^{-7}$
0.200	0.010	$5.4*10^{-7}$

Since the NH_4^{1+} concentration is consant in the first two experiments, the reaction order for NO_2^{1-} is:

$$\ln\left[\frac{1.35 \cdot 10^{-7} \cdot (mole \cdot liter^{-1} \cdot sec^{-1})}{2.75 \cdot 10^{-7} \cdot (mole \cdot liter^{-1} \cdot sec^{-1})}\right] = y \cdot \ln\left[\frac{0.005 \cdot (mole \cdot liter^{-1})}{0.01 \cdot (mole \cdot liter^{-1})}\right]$$

$$-.71149631922814184448 = y \cdot -.69314718055994530942$$

$$y := 1.0264722113611910597$$

Since the NO_2^{1-} concentration is constant in the last two experiments, the reaction order for NH_4^{1+} is:

$$\ln\left[\frac{2.75\cdot 10^{-7}\cdot\left(mole\cdot liter^{-1}\cdot sec^{-1}\right)}{5.4\cdot 10^{-7}\cdot\left(mole\cdot liter^{-1}\cdot sec^{-1}\right)}\right] = x\cdot\ln\left[\frac{0.1\cdot\left(mole\cdot liter^{-1}\right)}{0.2\cdot\left(mole\cdot liter^{-1}\right)}\right]$$

$$-.67479804189174877436 = x\cdot -.69314718055994530942$$

$$x := .97352778863880894029$$

Knowing the rate order, find k

First Experiment:

$$Rate = k\cdot C_{NH4}{}^{x}\cdot C_{NO2}{}^{y}$$

$$1.35\cdot 10^{-7}\cdot mole\cdot liter^{-1}\cdot sec^{-1} = k\cdot\left(0.100\cdot mole\cdot liter^{-1}\right)^{1}\cdot\left(0.0050\cdot mole\cdot liter^{-1}\right)^{1}$$

$$k := 2.7\cdot\frac{10^{-4}}{mole}\cdot\frac{liter}{sec}$$

Second Experiment:

$$Rate = k\cdot C_{NH4}{}^{x}\cdot C_{NO2}{}^{y}$$

$$2.75\cdot 10^{-7}\cdot mole\cdot liter^{-1}\cdot sec^{-1} = k\cdot\left(0.100\cdot mole\cdot liter^{-1}\right)^{1}\cdot\left(0.010\cdot mole\cdot liter^{-1}\right)^{1}$$

$$k := 2.75\cdot\frac{10^{-4}}{mole}\cdot\frac{liter}{sec}$$

Third Experiment:

$$Rate = k\cdot C_{NH4}{}^{x}\cdot C_{NO2}{}^{y}$$

$$5.4\cdot 10^{-7}\cdot mole\cdot liter^{-1}\cdot sec^{-1} = k\cdot\left(0.200\cdot mole\cdot liter^{-1}\right)^{1}\cdot\left(0.010\cdot mole\cdot liter^{-1}\right)^{1}$$

$$k := 2.7\cdot\frac{10^{-4}}{mole}\cdot\frac{liter}{sec}$$

The Rate Law for this reaction

$$rate = \left(2.7\cdot 10^{-4}\cdot liter\cdot mole^{-1}\cdot sec^{-1}\right)\cdot\left(C_{NH4}\right)^{1}\cdot\left(C_{NO2}\right)^{1}$$

For the reaction:

$NH4 + NO2- \rightarrow N2 + 2\ H2O$

The Rate Law for this reaction

$$rate = \left(2.7\cdot10^{-4}\cdot liter\cdot mole^{-1}\cdot sec^{-1}\right)\cdot\left(C_{NH4}\right)^{1}\cdot\left(C_{NO2}\right)^{1}$$

Determine the rate under different conditions:

$$C_{NH4} := \begin{bmatrix} 10^{-3} \\ 10^{-5} \\ 3\cdot10^{-2} \end{bmatrix}\cdot\frac{mole}{liter} \qquad C_{NO2} := \begin{bmatrix} 10^{-3} \\ 10^{-1} \\ 3\cdot10^{-3} \end{bmatrix}\cdot\frac{mole}{liter}$$

$$i := 0, 1 .. 2$$

$$rate_i := \left(2.7\cdot10^{-4}\cdot liter\cdot mole^{-1}\cdot sec^{-1}\right)\cdot\left(C_{NH4_i}\right)^{1}\cdot\left(C_{NO2_i}\right)^{1}$$

$$rate = \begin{bmatrix} 2.7\cdot10^{-10} \\ 2.7\cdot10^{-10} \\ 2.43\cdot10^{-8} \end{bmatrix}\circ mole\cdot liter^{-1}\cdot sec^{-1}$$