

## Chemistry 146 Lecture Problems Rate Law

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

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 unknown. One method for determining the rate constant (k) is to perform the experiment under two sets of experimental conditions so that:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k \cdot (A_1)^x \cdot (B_1)^y}{k \cdot (A_2)^x \cdot (B_2)^y}$$

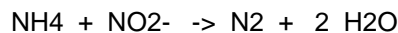
This experiment may be done two ways. By using a large excess of B, only A changes concentration. Or using initial rates for two different concentrations of A, with the same concentration of B. Since k and B are constant under these conditions:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{A_1^x}{A_2^x}$$

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \left( \frac{A_1}{A_2} \right)^x$$

$$\ln \left( \frac{\text{Rate}_1}{\text{Rate}_2} \right) = x \cdot \ln \left( \frac{A_1}{A_2} \right)$$

For the reaction:



With the following experimental data:

$[\text{NH}_4^{1+}]$ (M)	$[\text{NO}_2^{1-}]$ (M)	Rate (M sec <sup>-1</sup> )
0.100	0.0050	$1.35 \cdot 10^{-7}$
0.100	0.010	$2.75 \cdot 10^{-7}$
0.200	0.010	$5.4 \cdot 10^{-7}$

Since the  $\text{NH}_4^{1+}$  concentration is constant in the first two experiments, the reaction order for  $\text{NO}_2^{1-}$  is:

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

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

$$y := 1.0264722113611910597$$

Since the  $\text{NO}_2$  concentration is constant in the last two experiments, the reaction order for  $\text{NH}_4^+$  is:

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

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

$$x := .97352778863880894029$$

Knowing the rate order, find k

First Experiment:

$$\text{Rate} = k \cdot C_{\text{NH}_4}^x \cdot C_{\text{NO}_2}^y$$

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

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

Second Experiment:

$$\text{Rate} = k \cdot C_{\text{NH}_4}^x \cdot C_{\text{NO}_2}^y$$

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

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

Third Experiment:

$$\text{Rate} = k \cdot C_{\text{NH}_4}^x \cdot C_{\text{NO}_2}^y$$

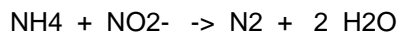
$$5.4 \cdot 10^{-7} \cdot \text{mole} \cdot \text{liter}^{-1} \cdot \text{sec}^{-1} = k \cdot (0.200 \cdot \text{mole} \cdot \text{liter}^{-1})^1 \cdot (0.010 \cdot \text{mole} \cdot \text{liter}^{-1})^1$$

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

The Rate Law for this reaction

$$\text{rate} = (2.7 \cdot 10^{-4} \cdot \text{liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}) \cdot (C_{\text{NH}_4})^1 \cdot (C_{\text{NO}_2})^1$$

For the reaction:



The Rate Law for this reaction

$$\text{rate} = (2.7 \cdot 10^{-4} \cdot \text{liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}) \cdot (\text{C}_{\text{NH}_4})^1 \cdot (\text{C}_{\text{NO}_2})^1$$

Determine the rate under different conditions:

$$\text{C}_{\text{NH}_4} := \begin{bmatrix} 10^{-3} \\ 10^{-5} \\ 3 \cdot 10^{-2} \end{bmatrix} \frac{\text{mole}}{\text{liter}} \quad \text{C}_{\text{NO}_2} := \begin{bmatrix} 10^{-3} \\ 10^{-1} \\ 3 \cdot 10^{-3} \end{bmatrix} \frac{\text{mole}}{\text{liter}}$$

$i := 0, 1, 2$

$$\text{rate}_i := (2.7 \cdot 10^{-4} \cdot \text{liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}) \cdot (\text{C}_{\text{NH}_4}_i)^1 \cdot (\text{C}_{\text{NO}_2}_i)^1$$

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