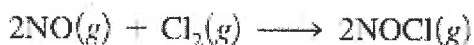


## CHEM 101B Kinetics – Initial Rates Method for determining Rate Law

29. The reaction



was studied at  $-10^\circ\text{C}$ . The following results were obtained where

$$\text{Rate} = -\frac{\Delta[\text{Cl}_2]}{\Delta t}$$

|    | [NO] <sub>0</sub><br>(mol/L) | [Cl <sub>2</sub> ] <sub>0</sub><br>(mol/L) | Initial Rate<br>(mol/L · min) |
|----|------------------------------|--|-------------------------------|
| 1) | 0.10                         | 0.10                                       | 0.18                          |
| 2) | 0.10                         | 0.20                                       | 0.36                          |
| 3) | 0.20                         | 0.20                                       | 1.45                          |

1<sup>st</sup> order in [Cl<sub>2</sub>]  
2<sup>nd</sup> order in [NO]

$$\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$$

- What is the rate law?
- What is the value of the rate constant?

~~exp 1 & exp 2~~

$$\frac{\text{exp 2}}{\text{exp 1}} = \frac{[\text{Cl}_2]^n}{[\text{Cl}_2]^n} = \frac{\text{rate}}{\text{rate}}$$

$$\left(\frac{.20}{.10}\right)^n = \left(\frac{.36}{.18}\right)$$

$$2^n = 2 \quad \log_2 2 = n$$

$$n = 1 \quad 1 = n$$

$$\frac{\text{exp 1}}{\text{exp 3}}$$

$$\frac{[\text{NO}]^n}{[\text{NO}]^n} = \frac{\text{rate}}{\text{rate}}$$

$$\left(\frac{.10}{.20}\right)^n = \frac{.18}{1.45}$$

$$.5^n = 0.124$$

$$\log_{.5}(.124) = n$$

$$\frac{\log(.124)}{\log(.5)} = n$$

$$3.01 = n \quad (2+1)$$

$$n = 3$$

$$\text{rate} = k \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NO}]^2 [\text{Cl}_2]}$$

$$1) \quad k = \frac{\text{rate}}{[\text{NO}]^2 [\text{Cl}_2]} = \frac{.18}{(.10)^2 (.10)} = 180$$

$$2) \quad \frac{.36}{(.10)^2 (.20)} = 180$$

$$3) \quad \frac{1.45}{(.20)^2 (.20)} = 181$$

$$k = 180 \text{ (value)}$$

k (unit)

$$k = \frac{\text{rate}}{[\text{NO}]^2 [\text{Cl}_2]} = \frac{\frac{\text{mol}}{\text{L} \cdot \text{min}}}{\left(\frac{\text{mol}}{\text{L}}\right)^2 \left(\frac{\text{mol}}{\text{L}}\right)} = \frac{\frac{1}{\text{min}}}{\frac{\text{mol}^3}{\text{L}^3}} = \frac{\text{L}^3}{\text{mol}^3 \cdot \text{min}}$$

$$= \frac{\frac{\text{M}}{\text{min}}}{\text{M}^2 \cdot \text{M}} = \frac{1}{\text{min}} = \frac{1}{\text{M}^2 \cdot \text{min}}$$

30. The reaction



was studied at 25°C. The following results were obtained where

$$\text{Rate} = -\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t}$$

|   | $[\text{I}^-]_0$<br>(mol/L) | $[\text{S}_2\text{O}_8^{2-}]_0$<br>(mol/L) | Initial Rate<br>(mol/L · s) |
|---|-----------------------------|--|-----------------------------|
| 1 | 0.080                       | 0.040                                      | $12.5 \times 10^{-6}$       |
| 2 | 0.040                       | 0.040                                      | $6.25 \times 10^{-6}$       |
| 3 | 0.080                       | 0.020                                      | $6.25 \times 10^{-6}$       |
| 4 | 0.032                       | 0.040                                      | $5.00 \times 10^{-6}$       |
| 5 | 0.060                       | 0.030                                      | $7.00 \times 10^{-6}$       |

- a. Determine the rate law.  $\text{rate} = k[\text{I}^-][\text{S}_2\text{O}_8^{2-}]$   
 b. Calculate a value for the rate constant for each experiment and an average value for the rate constant.

$$\frac{1}{2} [\text{I}^-] \quad \left(\frac{0.040}{0.080}\right)^n = \frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}}$$

$$2^n = 2 \quad n = 1$$

$$\frac{1}{3} [\text{S}_2\text{O}_8^{2-}] \quad \left(\frac{0.040}{0.020}\right)^n = \frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}}$$

$$2^n = 2 \quad n = 1$$

$$k = \frac{\text{rate}}{([\text{I}^-][\text{S}_2\text{O}_8^{2-}])}$$

1)  $3.9 \times 10^{-3}$

2)  $3.9 \times 10^{-3}$

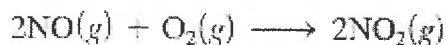
3)  $3.9 \times 10^{-3}$

4)  $3.9 \times 10^{-3}$

5)  $3.9 \times 10^{-3}$

Avg  $k = 3.9 \times 10^{-3}$

34. The reaction



was studied, and the following data were obtained where

$$\text{Rate} = -\frac{\Delta[\text{O}_2]}{\Delta t}$$

|    | [NO] <sub>0</sub><br>(molecules/cm <sup>3</sup> ) | [O <sub>2</sub> ] <sub>0</sub><br>(molecules/cm <sup>3</sup> ) | Initial Rate<br>(molecules/cm <sup>3</sup> · s) |
|----|---|--|---|
| 1) | 1.00 × 10 <sup>13</sup>                           | 1.00 × 10 <sup>13</sup>  | 2.00 × 10 <sup>16</sup>                         |
| 2) | 3.00 × 10 <sup>13</sup>                           | 1.00 × 10 <sup>13</sup>  | 1.80 × 10 <sup>17</sup>                         |
| 3) | 2.50 × 10 <sup>13</sup>                           | 2.50 × 10 <sup>13</sup>  | 3.13 × 10 <sup>17</sup>                         |

What would be the initial rate for an experiment where [NO]<sub>0</sub> = 6.21 × 10<sup>13</sup> molecules/cm<sup>3</sup> and [O<sub>2</sub>]<sub>0</sub> = 7.36 × 10<sup>13</sup> molecules/cm<sup>3</sup>?

$$\frac{\text{exp 3}}{\text{exp 1}} \left( \frac{3.00 \times 10^{13}}{1.00 \times 10^{13}} \right)^n = \frac{1.80 \times 10^{17}}{2.00 \times 10^{16}}$$

$$3.00^n = 9.00$$

$$n = 2$$

$$\log 3^9 = n$$

$$\frac{\log 9}{\log 3} = n$$

$$2 = n$$

$$\frac{\text{exp 3}}{\text{exp 2}} \left( \frac{2.50 \times 10^{13}}{3.00 \times 10^{13}} \right)^2 \left( \frac{2.50 \times 10^{13}}{1.00 \times 10^{13}} \right)^n = \frac{3.13 \times 10^{17}}{1.80 \times 10^{17}}$$

$$0.694 (2.50)^n = 1.74$$

$$2.50^n = 2.504$$

$$n = 1$$

$$\text{rate} = k [\text{NO}]^2 [\text{O}_2]$$

$$1) k = \frac{\text{rate}}{[\text{NO}]^2 [\text{O}_2]} = 2.00 \times 10^{-38}$$

$$= 2.00 \times 10^{-38}$$

$$= 2.00 \times 10^{-38}$$

$$\text{rate} = (2.00 \times 10^{-38}) (6.21 \times 10^{13})^2 (7.36 \times 10^{13})$$

$$= 5.69 \times 10^{18} \frac{\text{molecules}}{\text{cm}^3 \cdot \text{s}}$$

35. The rate of the reaction between hemoglobin (Hb) and carbon monoxide (CO) was studied at 20°C. The following data were collected with all concentration units in  $\mu\text{mol/L}$ . (A hemoglobin concentration of  $2.21 \mu\text{mol/L}$  is equal to  $2.21 \times 10^{-6} \text{ mol/L}$ .)

| $[\text{Hb}]_0$<br>( $\mu\text{mol/L}$ ) | $[\text{CO}]_0$<br>( $\mu\text{mol/L}$ ) | Initial Rate<br>( $\mu\text{mol/L} \cdot \text{s}$ ) |
|--|--|--|
| 2.21                                     | 1.00                                     | 0.619  |
| 4.42                                     | 1.00                                     | 1.24   |
| 4.42                                     | 3.00                                     | 3.71   |

- a. Determine the orders of this reaction with respect to Hb and CO.
- b. Determine the rate law.
- c. Calculate the value of the rate constant.
- d. What would be the initial rate for an experiment with  $[\text{Hb}]_0 = 3.36 \mu\text{mol/L}$  and  $[\text{CO}]_0 = 2.40 \mu\text{mol/L}$ ?

1st in both

$$\text{rate} = k[\text{Hb}]_0[\text{CO}]$$

$$\left. \begin{array}{l} .280 \\ .281 \\ .280 \end{array} \right) .280$$

$$\begin{aligned} \text{rate} &= .280(3.36)(2.40) \\ &= \boxed{2.26 \mu\text{mol/L} \cdot \text{s}} \end{aligned}$$