Tutorial 6

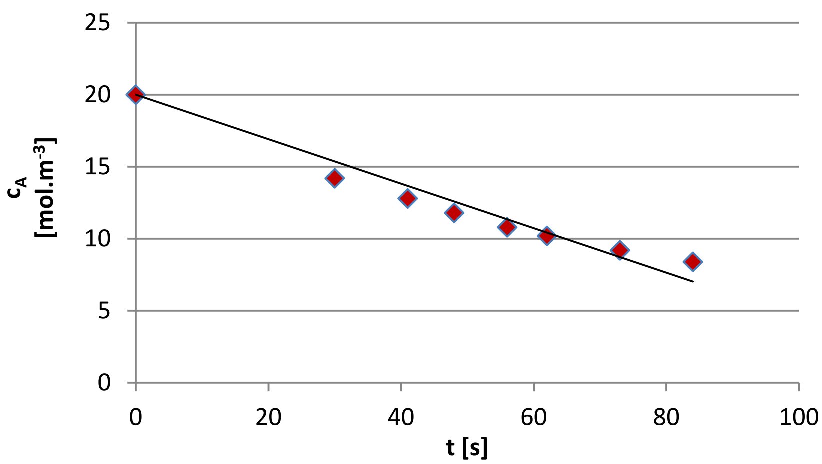
Question 2

1) <u>0^{th} order w.r.t. A & B</u>:

$$\frac{dC_A}{dt} = r_A = -k_1$$

$$C_A = -k_1 t + C_{A0}$$

Plot of C_A vs. time gives:



→ k_1 = 0.1546 $mol.m^{-3}.s^{-1}$

→ R^2 = 0.9451

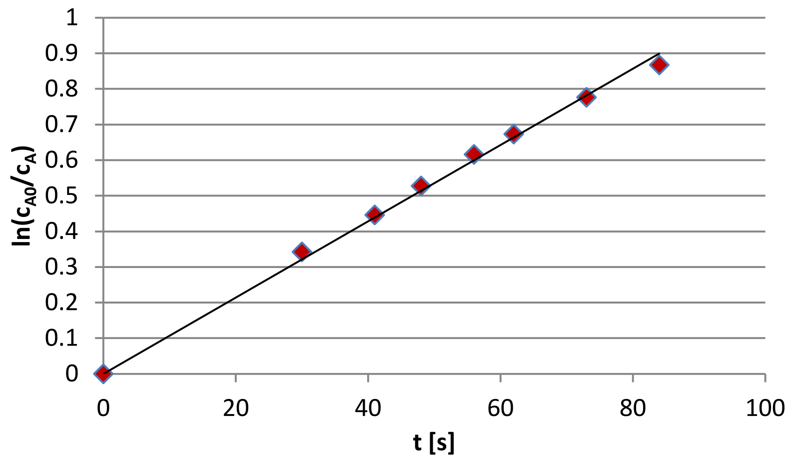
Better line can be fitted to these data. Therefore, it is concluded that the reaction is not a zero order with respect to A or B.

2) <u>1^{st} order w.r.t. A & 0^{th} order w.r.t. B</u>:

$$\frac{dC_A}{dt} = r_A = -k_2 C_A$$

$$ln\left(\frac{C_{A0}}{C_A}\right) = k_2 t$$

Plot of $ln(C_{A0}/C_A)$ vs. t is:



→ $k_2 = 0.0107\ s^{-1}$

→ $R^2 = 0.9960$

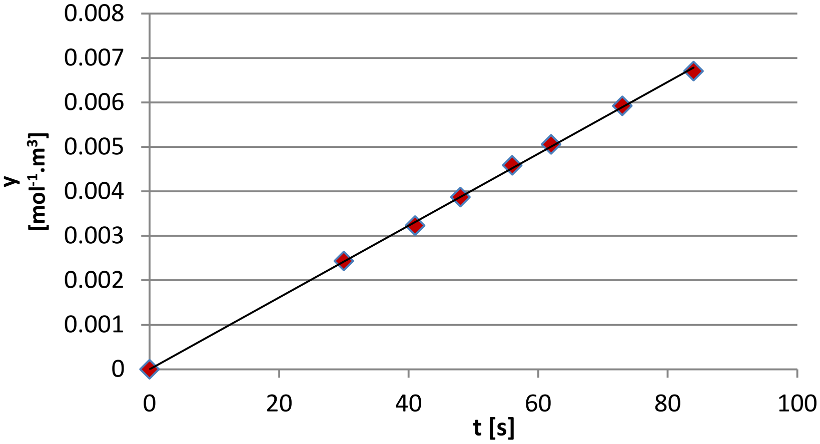
The data does appear to be randomly assorted around the line of best fit, which supports the idea that the reaction is first order with respect to A, but let's check the reaction order with respect to B.

3) 1^{st} order w.r.t. A & B:

$$\frac{dC_A}{dt} = r_A = -k_3 C_A C_B$$

$$\frac{1}{(\theta_B - 3)C_{A0}} \ln\left(\frac{1 - \frac{3X_A}{\theta_B}}{1 - X_A}\right) = y = k_3 t$$

Plot of "y" vs. t gives:



→ $k_3 = 8.07 \times 10^{-5}$ mol^{-1}.m^3.s^{-1}

→ $R^2 = 0.9994$

It is immediately evident that the line is a very good fit ($R^2 = 0.999$), and the data points are randomly scattered about the line, indicating an appropriate model. Thus, the reaction appears to be first order with respect to both ethylene dibromide (A) and potassium iodide (B). The rate constant is therefore approximated as 8.07×10^{-5} mol^{-1}.m^3.s^{-1}

Question 3

1) Operating the experiment with **species B in excess**:

$$c_B \cong c_{B0} = 8\ mol.L^{-1}$$

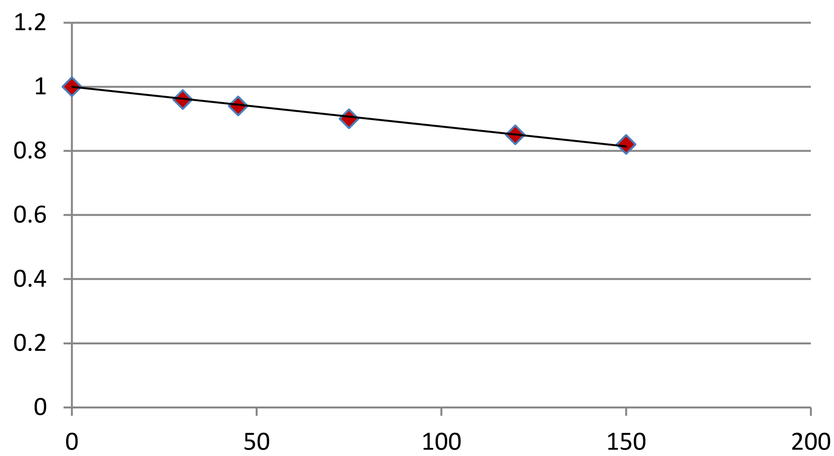
Using the method of excess:

$$-r_A = k'_A C_A^{\alpha} \quad \text{where} \quad k'_A = k_A C_{B0}^{\beta}$$

if $\underline{\alpha = 0}$:

$$C_A = -k'_A t + C_{A0}$$

Plot of C_A vs. t:



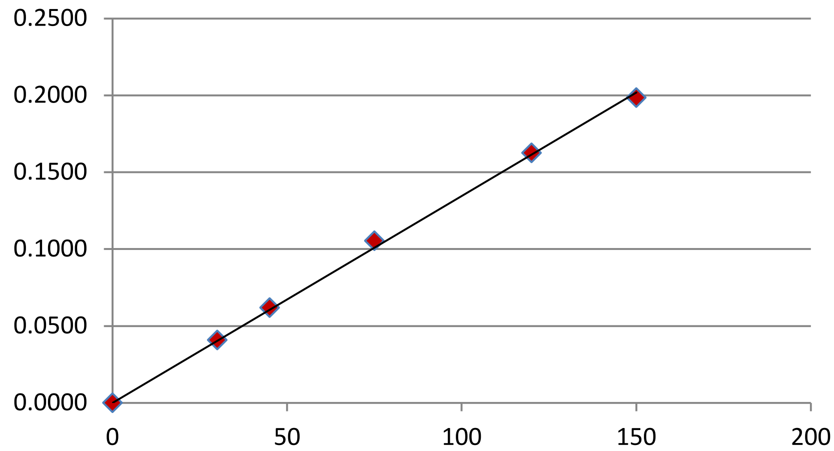
→ k'_A= 1.24 × 10^{-3} mol.L^{-1}.s^{-1}

→ R^2 = 0.9952

if $\underline{\alpha = 1}$:

$$ln\left(\frac{C_{A0}}{C_A}\right) = k'_A t$$

Plot of $ln(c_{A0}/c_A)$ vs. t :



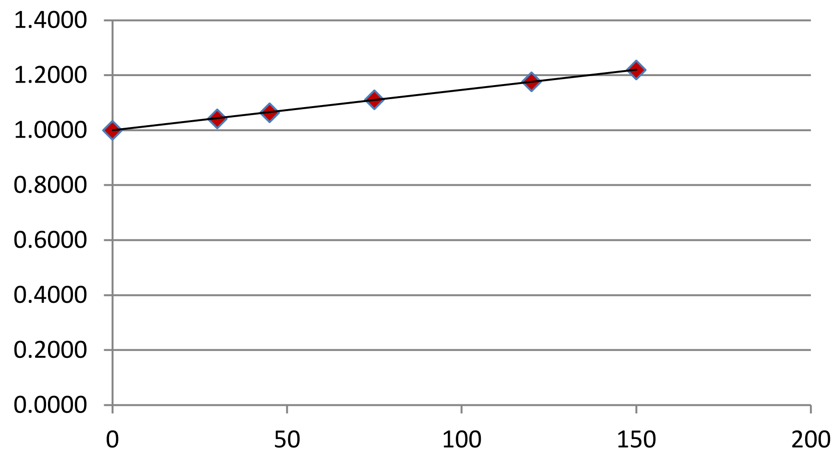
→ $k'_A = 1.35 \times 10^{-3}\ s^{-1}$

→ $R^2 = 0.9988$

if $\alpha = 2$:

$$\frac{1}{C_A} = k'_A t + \frac{1}{C_{A0}}$$

Plot of $(1/c_A)$ vs. t :



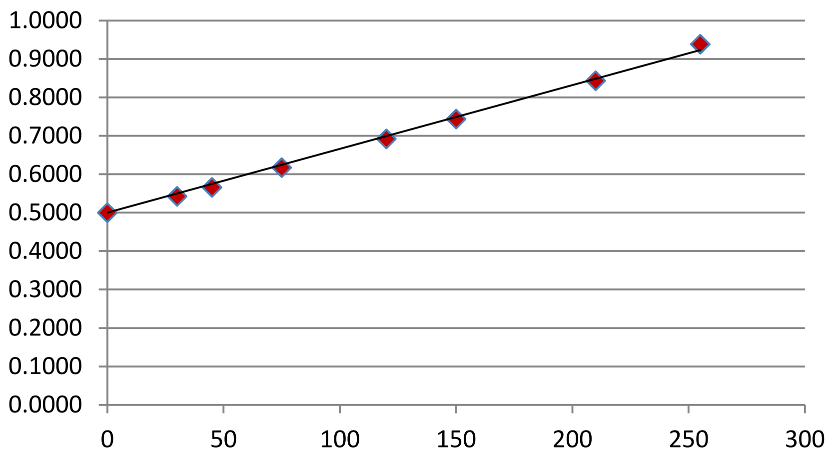
→ k'_A= 1.46 × 10^{-3} $mol^{-1}.L.s^{-1}$

→ R^2 = 0.9997

if $\alpha = 3$:

$$\frac{1}{2C_A^2} = k'_A t + \frac{1}{2C_{A0}^2}$$

Plot of ($c_A^{-2}/2$) vs. t is:



→ k'_A= 1.66 × 10^{-3} $mol^{-2}.L^2.s^{-1}$

→ R^2 = 0.9970

The second-order case displays the best linearity, thus the coefficient α is assumed to be 2. For this case, the lumped rate constant (k'_A) is determined to be approximately 1.46 × 10^{-3} $mol^{-1}.L.s^{-1}$

2) Operating the experiment with **species A in excess**:

$$C_A \cong C_{A0} = 15\ mol.L^{-1}$$

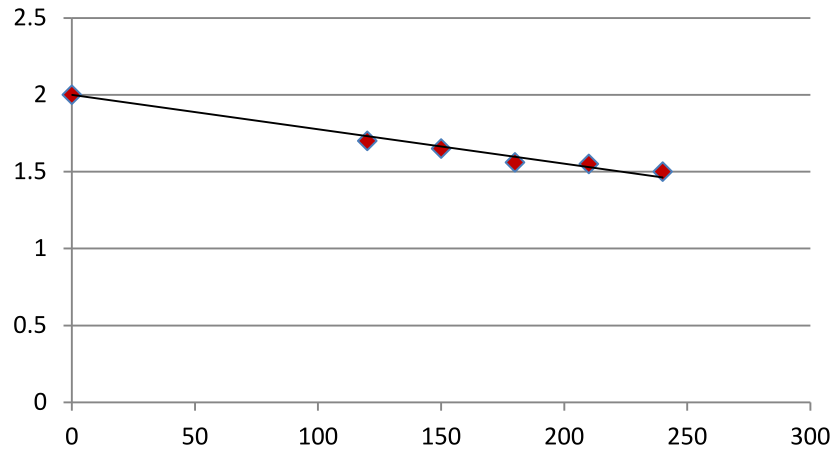
Using the method of excess:

$$-r_A = k''_A C_B^{\beta} \quad \text{where} \quad k''_A = k_A C_{A0}^{\alpha}$$

if $\underline{\beta = 0:}$

$$C_B = -k''_A t + C_{B0}$$

Plot of C_A vs. t is:



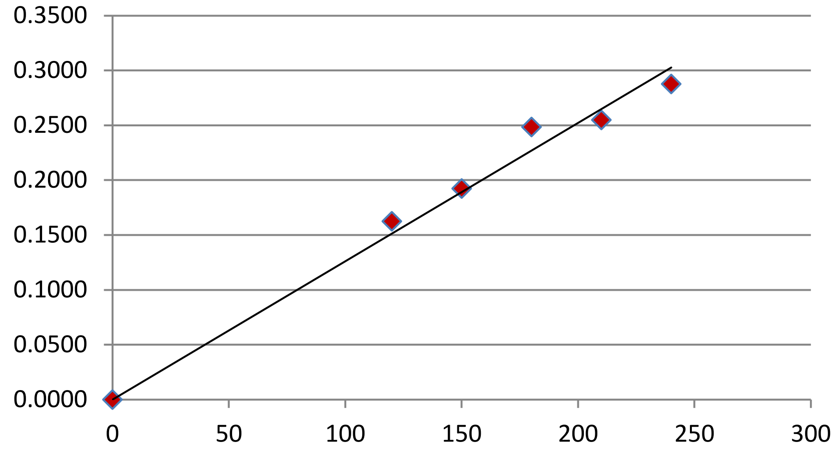
→ $k''_A = 2.24 \times 10^{-3}$ mol.L^{-1}.s^{-1}

→ $R^2 = 0.9736$

if $\underline{\beta = 1:}$

$$ln\left(\frac{C_{B0}}{C_B}\right) = k''_A t$$

Plot of $ln(C_{B0}/C_B)$ vs. t is:



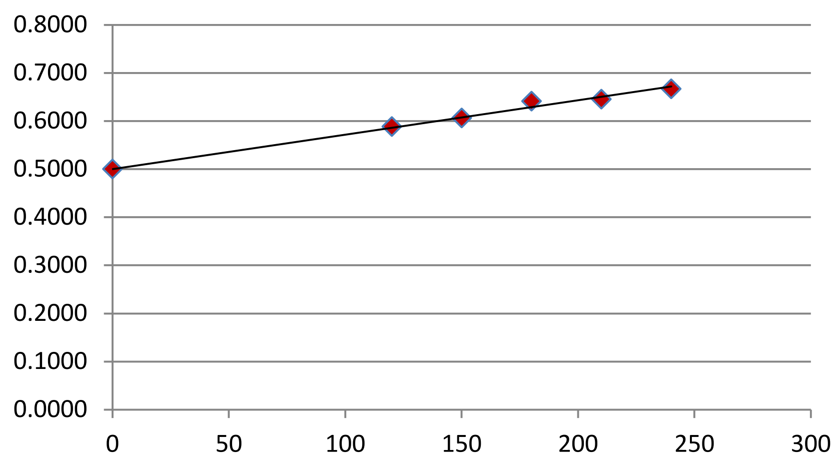
→ k''_A= 1.26 × 10^{-3} s^{-1}

→ R^2 = 0.9830

if $\underline{\beta = 2:}$

$$\frac{1}{C_B} = k''_A t + \frac{1}{C_{B0}}$$

Plot of ($1/c_B$) vs. t gives:



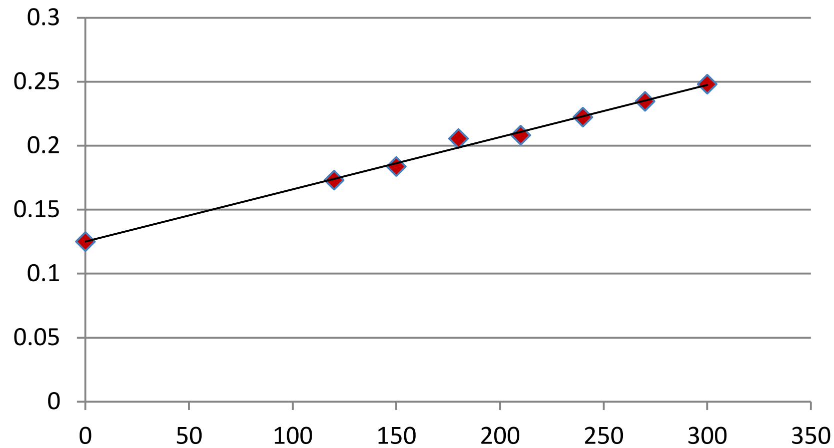
→ k''_A= 7.16 × 10^{-4} $mol^{-1}.L.s^{-1}$

→ $R^2 = 0.9884$

if $\underline{\beta = 3:}$

$$\frac{1}{2C_B^2} = k''_A t + \frac{1}{2C_{B0}^2}$$

Plot of ($C_B^{-2}/2$) vs. t is:



→ $k''_A = 4.08 \times 10^{-4}$ $mol^{-2}.L^2.s^{-1}$

→ $R^2 = 0.9940$

The third-order case displays the best linearity, thus the coefficient β is assumed to be 3. For this case, the lumped rate constant (k''_A) is determined to be approximately 4.08×10^{-4} $mol^{-4}.L^2.s^{-1}$

3)

From definition: $k_A = \frac{k''_A}{C_{A0}^{\alpha}}$ as well as $k_A = \frac{k'_A}{C_{B0}^{\beta}}$

Use the average value:

$$k_A = \frac{1}{2}\left(\frac{k''_A}{C_{A0}^{\alpha}} + \frac{k'_A}{C_{B0}^{\beta}}\right) = \frac{1}{2}\left(\frac{(4.08 \times 10^{-4}\ \mathrm{mol}^{-2}.\mathrm{L}^{2}.\mathrm{s}^{-1})}{(15\ mol.L^{-1})^{2}} + \frac{(1.46 \times 10^{-3}\ \mathrm{mol}^{-1}.\mathrm{L}.\mathrm{s}^{-1})}{(8\ mol.L^{-1})^{3}}\right)$$

$$\therefore k_A \cong 2.33 \times 10^{-6}\ \mathrm{mol}^{-4}\mathrm{L}^{4}\mathrm{s}^{-1}$$

Thus, the constants of the rate expression can be approximated as:

$\alpha = 2$

$\beta = 3$

$k_A = 2.33 \times 10^{-6}\ \mathrm{mol}^{-4}\mathrm{L}^{4}\mathrm{s}^{-1}$

$$r_A \cong (2.33 \times 10^{-6}\ \mathrm{mol}^{-4}\mathrm{L}^{4}\mathrm{s}^{-1})\ c_A^{2} c_B^{3}$$