Exercise 9:

Express \( n_A \) and \( n_B \) in terms of fractional conversion of \( \Delta \) (\( f_A \)).

\[
\begin{align*}
    n_A &= n_A^0 - n_A^0 \cdot f_A \\
    n_B &= n_B^0 - 2n_A^0 \cdot f_A
\end{align*}
\]  
(1)  
(2)

For constant density (\( \rho \)), and constant volume (\( V \)), \( \frac{n}{\rho} \) can be expressed as concentration (\( C \)).

\[
\begin{align*}
    C_A &= C_A^0 - C_A^0 \cdot f_A = C_A^0 \left( 1 - f_A \right) \\
    C_B &= C_B^0 - 2C_A^0 \cdot f_A \\
    C_B &= C_B^0 (3 - 2f_A)
\end{align*}
\]  
(3)  
(4)  
(5)

Substitute equations (3) and (5) into the given rate expression.

\[
\frac{dC_A}{dt} = \frac{d(C_A^0 - C_A^0 \cdot f_A)}{dt} = -C_A^0 \cdot \frac{df_A}{dt} = -\frac{dC_A}{C_A} = -\frac{C_A}{C_A} \frac{dl}{l} \cdot \frac{dl}{l}
\]  
(6)

\[
\frac{df_A}{dt} = \frac{kC_A C_A^{-1}}{C_A^0} = kC_A^0 \left( 1 - f_A \right)(3 - 2f_A)^2
\]  
(7)

Separate variables and integrate.

\[
\int_{0}^{t} \frac{df_A}{(1 - f_A)(3 - 2f_A)^2} = \int_{0}^{t} \frac{kC_A^0}{dt}
\]  
(8)

Solving for the rate constant (\( k \)) gives \( k = 120 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1} \).
Exercise 13:

Write the rate expression for DEBA, assuming constant volume.

\[ r = \frac{dC_{DEBA}}{dt} = kC_{DEBA}C_{BA} \]  

(1)

Find \( C_{DEBA} \) and \( C_{BA} \) in terms of \( C_{DEBA}^o \) and \( C_{BA}^o \):

\[ C_{DEBA} = C_{DEBA}^o + \left( \frac{1}{1} \right) \left( C_{DEBA}^o - C_{DEBA}^o \right) \]  

(2)

\[ C_{BA} = C_{BA}^o + \left( \frac{1}{1} \right) \left( C_{DEBA}^o - C_{DEBA}^o \right) \]  

(3)

Substitute equations (2) and (3) into equation (1), using the initial conditions given for 1,4-butanediol and acetonitrile, respectively.

\[ \frac{dC_{DEBA}}{dt} = k(0.5 - C_{DEBA})(0.5 - C_{DEBA}) \]  

(4)

\[ \frac{dC_{DEBA}}{dt} = k(1 - C_{DEBA})(0.1 - C_{DEBA}) \]  

(5)

Rearrange equations (4) and (5), and integrate to find \( C_{DEBA} \) as a function of time for each solvent.

1,4-butanediol:

\[ \int_{0}^{t} \frac{dC_{DEBA}}{(0.5 - C_{DEBA})} = \int_{0}^{t} k \cdot dt \]  

\[ \frac{1}{0.5 - C_{DEBA}} = kt + 2 \]  

(7)

acetonitrile:

\[ \int_{0}^{t} \frac{dC_{DEBA}}{(1 - C_{DEBA})(0.1 - C_{DEBA})} = \int_{0}^{t} k \cdot dt \]  

\[ \ln \frac{1 - C_{DEBA}}{1 - 0.1C_{DEBA}} = \frac{9 \cdot kt}{10} \]  

(9)

Using equations (7) and (9), find the rate constant \( k \) for each solvent.

1,4-butanediol: \( k = 0.000212 \text{ L mol}^{-1} \text{ min}^{-1} \)

acetonitrile: \( k = 0.00160 \text{ L mol}^{-1} \text{ min}^{-1} \)