Tyler Bradley | ENVE 660 | HW #2 | 1/28/18

(1) riboflavin + light $\rightarrow$ $^1O_2$
fructose + light $\rightarrow$ $^1O_2$

~~Assumption~~. Given: $V\frac{dC_{^1O_2}}{dt} = 0 \rightarrow [^1O_2] = \text{constant}$

$[^1O_2] = 10 \times 10^{-12}$ M

$^1O_2 + FFA \xrightarrow{k} X$

$r_{FFA} = -k\,C_{FFA}\,C_{^1O_2}$

t [=] min	C_{FFA} [=] M
0	4×10^{-5}
10	2.43×10^{-5}
20	1.48×10^{-5}
30	8.98×10^{-6}
40	5.46×10^{-6}
50	3.32×10^{-6}
60	2.02×10^{-6}

$$\cancel{V}\frac{dC_{FFA}}{dt} = \cancel{V} r_{FFA} = -k C_{FFA} C_{O_2} \cancel{V}$$

$$\int_{C_{FFA,0}}^{C_{FFA,t}} \frac{dC_{FFA}}{C_{FFA}} = \int_0^t -k C_{O_2}\,dt \Rightarrow \ln C_{FFA}\Big]_{C_{FFA,0}}^{C_{FFA,t}} = -k C_{O_2} t\Big]_0^t$$

$$\ln C_{FFA,t} - \ln C_{FFA,0} = -k C_{O_2} t$$

$$\ln C_{FFA,t} = -k C_0 t + \ln C_{FFA,0}$$

$\rightarrow$ plot $\ln C_{FFA,t}$ vs t (shown on attached print out w/ R code)

slope $= -kC_0 = -0.0498$

intercept $= \ln C_{FFA,0} = -10.1$

$$-kC_0 = -0.0498$$

$$k = 0.0498 / 10 \times 10^{-12}\text{ M} = \boxed{4.98 \times 10^{9}}$$

```
#============================================================================
#graph for hw 2 - number 1
#
# Tyler Bradley
# 1/28/2018
#============================================================================
```

Loading required libraries

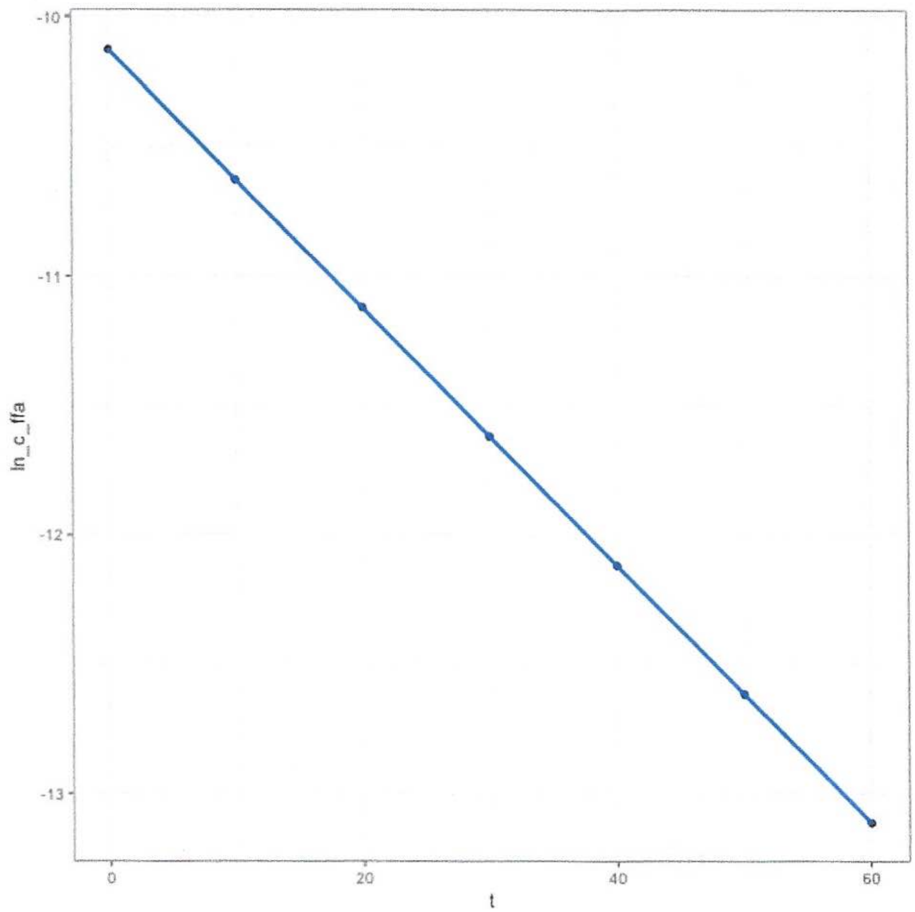
```
library(tidyverse)
library(broom)
```

Creating dataset from problem

```
ffa_data <- tribble(
  ~t,    ~c_ffa,
  0,     4e-5,
  10,    2.43e-5,
  20,    1.48e-5,
  30,    8.98e-6,
  40,    5.46e-6,
  50,    3.32e-6,
  60,    2.02e-6
) %>%
  # adding ln(C_ffa) column
  # log() function in R defaults to ln
  mutate(ln_c_ffa = log(c_ffa))
```

Plotting the log concentration of FFA vs time

```
ggplot(ffa_data, aes(t, ln_c_ffa)) +
  geom_point() +
  geom_smooth(method = "lm") +
  theme_bw()
```



Running linear model to get slope and intercept values.

```
ffa_model <- ffa_data %>%
  nest() %>%
  mutate(lm_model = map(data, ~lm(ln_c_ffa ~ t, data = .x)),
         lm_tidy = map(lm_model, tidy))

# Printing linear model coeffecients.
ffa_model %>% unnest(lm_tidy, .drop = TRUE) %>% knitr::kable()
```

term	estimate	std.error	statistic	p.value
(Intercept)	-10.1267742	0.0005306	-19087.002	0
t	-0.0497698	0.0000147	-3382.239	0

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② $A + B + C \rightarrow P$

$$r_c = -k C_A^{1.2} C_B^{1.8} C_c^{2}$$

Assumptions:
- Batch reactor → no advection, dispersion, diffusion
- $C_A >> C_c$ → C_A is constant
- $C_B >> C_c$ → C_B = constant

$C_{A,0} = 150$ mg/L ; $C_{B,0} = 130$ mg/L

$C_{c,0} = 0.10$ mg/L ; $t_{1/2} = 28$ mins

a) what is overall rxn rate?

↳ sum exponents = $1.2 + 1.8 + 2 = 5$ ⇒ $\boxed{5^{th} \text{ order rxn}}$

b) what is k?

↳ since C_A & C_B are constant → r_c can be treated as psuedo-second order

$$r_c = -kC_A^{1.2} C_B^{1.8} C_c^2 = -k^* C_c^2$$

$$k^* = k C_A^{1.2} C_B^{1.8}$$
$$= k(150)^{1.2}(130)^{1.8} = 2.61 \times 10^6 \, k$$

$$\cancel{V}\frac{dC_c}{dt} = \cancel{V} r_c = -k^* C_c^2$$

$$\int_{C_{c0}}^{C_{c,t}} -\frac{dC_c}{C_c^2} = \int_0^t k^* dt$$

$$\frac{1}{C_{c,t}} - \frac{1}{C_{c,0}} = k^* t$$

@ $t = t_{1/2}$ ⇒ $C_{c,t} = \frac{1}{2} C_{c,0}$

$$\frac{1}{\frac{1}{2}C_{c,0}} - \frac{1}{C_{c,0}} = \frac{2}{C_{c,0}} - \frac{1}{C_{c,0}} = k^* t_{1/2}$$

$$\frac{1}{C_{c,0}} = k^* t_{1/2}$$

$$k^* = \frac{1}{C_{c,0}\, t_{1/2}} = \frac{1}{(0.10)(28 \text{ mins})} = 0.357 \frac{L}{mg \cdot mins}$$

↳ plugging into eq. for k^*

$$k^* = \left(2.61 \times 10^6 \frac{mg^3}{L^3}\right) k$$

$$k = k^* \Big/ \left(2.61 \times 10^6 \frac{mg^3}{L^3}\right) = \left(0.357 \frac{L}{mg \cdot mins}\right) \Big/ \left(2.61 \times 10^6 \frac{mg^3}{L^3}\right)$$

$$\boxed{k = 1.37 \times 10^{-7} \frac{L^4}{mg^4 \cdot min}}$$

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③ $A \xrightarrow{k_a} B \xrightarrow{k_b} C$

*based on k values, both r_A and r_B are 1st order

$C_{B,t=30} = ?$ $k_a = 2 \times 10^{-2} \frac{1}{min}$

$C_{A,0} = 5 \ mg/L$ $k_b = 0.5 \frac{1}{min}$

$C_{B,0} = C_{C,0} = 0 \ mg/L$

$$\cancel{V}\frac{dC_A}{dt} = \cancel{V} r_A = -k_a C_A$$

$$\cancel{V}\frac{dC_B}{dt} = \cancel{V} r_A + \cancel{V} r_B = k_a C_A - k_b C_B$$

$$\cancel{V}\frac{dC_C}{dt} = \cancel{V} r_B = k_b C_B$$

$$\int_{C_{A,0}}^{C_{A,t}} \frac{dC_A}{C_A} = \int_0^t -k_A \, dt$$

$$\ln C_{A,t} - \ln C_{A,0} = -k_A t$$

$$\exp\left[\ln\left(\frac{C_{A,t}}{C_{A,0}}\right)\right] = \exp\left[-k_A t\right]$$

$$C_{A,t} = C_{A,0} \exp(-k_A t)$$

Laplace Transforms used

$$\mathcal{L}(f(t)) = F(s)$$

$$\mathcal{L}(f'(t)) = sF(s) - f(0)$$

$$\mathcal{L}(\exp(-k_a t)) = \left(\frac{1}{s+k_a}\right)$$

$$\mathcal{L}^{-1}\left(\left(\frac{1}{s+a}\right)\left(\frac{1}{s+b}\right)\right) = \frac{e^{-at} - e^{-bt}}{b-a}$$

$$\mathcal{L}^{-1}(F(s)) = f(t)$$

$C_B = f(t)$

$\frac{dC_B}{dt} = f'(t)$

$$\frac{dC_B}{dt} = k_a C_A - k_b C_B$$

$$= k_a C_{A,0} \exp(-k_A t) - k_b C_B$$

$$= C_{A,0}(k_a)\exp(-k_a t) - k_b C_B$$

$$sF(s) - f(0) = C_{A,0} \, k_a \left(\frac{1}{s+k_a}\right) - k_b F(s)$$

$$sF(s) + k_b F(s) = C_{A,0} \, k_a \left(\frac{1}{s+k_a}\right) + \cancel{f(0)}^{0}$$

$$F(s)(s+k_b) = C_{A,0} \, k_A \left(\frac{1}{s+k_a}\right)$$

$$F(s) = C_{A,0} \, k_a \left(\frac{1}{s+k_a}\right)\left(\frac{1}{s+k_b}\right)$$

→ let $k_a = a$, $k_b = b$

$$F(s) = C_{A,0} \, k_a \left(\frac{1}{s+a}\right)\left(\frac{1}{s+b}\right)$$

$$C_B = C_{A,0} \, k_a \left(\frac{e^{-k_a t} - e^{-k_b t}}{k_b - k_a}\right)$$

$$C_B = (5 \ mg/L)\left(2 \times 10^{-2} \tfrac{1}{min}\right)\left(\frac{e^{-(2\times10^{-2}\frac{1}{m})(30 \ min)} - e^{-(0.5\frac{1}{m})(30 \ min)}}{0.5 \frac{1}{min} - 2 \times 10^{-2} \frac{1}{min}}\right)$$

$$= \left(0.1 \ \tfrac{mg}{L \cdot min}\right)(1.14 \ min)$$

$$\boxed{C_B = 0.114 \ mg/L}$$

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4:3-8 $4Mn^{2+} + O_2 + 6H_2O \longrightarrow 4MnOOH(s) + 8H^+$

$r_{Mn^{2+}} = -k\, C_{Mn^{2+}} C_{O_2}$

$k = 1.22\times10^{-2} \frac{1}{M\cdot s}\left(\frac{3600\ s}{1\ hr}\right)\left(\frac{24\ hr}{1\ day}\right) = 1054.08 \frac{1}{M\cdot days}$

$C_{O_2,0} = (2\ mg/L)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol}{32\ g}\right) = 6.25\times10^{-5}\ M$

a)

$C_{Mn^{2+},0} = (0.5\ mg/L)\left(\frac{1\ g}{1000\ mg}\right)\left(\frac{1\ mol}{54.938\ g}\right) = 9.101\times10^{-6}\ M$

from problem intro:

$$C_A(t) = \frac{C_{A,0} - \frac{a}{b}C_{B,0}}{1-\left(\frac{a}{b}\right)\left(\frac{C_{B,0}}{C_{A,0}}\right)\left\{\exp\left[-\left(\frac{bC_{A,0}}{aC_{B,0}}-1\right)C_{B,0}kt\right]\right\}}$$

$a = 4,\ b = 1,\ C_{A,0} = 9.101\times10^{-6}\ M$
$C_{B,0} = 6.25\times10^{-5}\ M$
$k = 1054.08 \frac{1}{M\cdot days}$

$$C_{Mn^{2+}}(t) = \frac{9.101\times10^{-6}\ M - \left(\frac{4}{1}\right)6.25\times10^{-5}\ M}{1-\left(\frac{4}{1}\right)\left(\frac{6.25\times10^{-5}\ \cancel{M}}{9.101\times10^{-6}\ \cancel{M}}\right)\left\{\exp\left[-\left(\frac{9.101\times10^{-6}\ \cancel{M}}{4(6.25\times10^{-5}\ \cancel{M})}-1\right)(6.25\times10^{-5}\ \cancel{M})\left(1054.08\frac{1}{M\cdot day}\right)t\right]\right\}}$$

$$C_{Mn^{2+}}(t) = \frac{-2.409\times10^{-4}\ M}{1-27.47\exp\left(0.635\frac{1}{day}\cdot t\right)}$$

↳ graph created in R and shown on attached page w/ R code

(i) @ what t does $C_{Mn}(t) = 20\ \mu g/L$

↳ from graph and calculated table: $t = 50$ days

(ii) characteristic rxn time according to first definition

$n = 2$

$$t_{char} = \frac{e-1}{k_2 C_B(0)} = \frac{1.718}{\left(1054.08\frac{1}{M\cdot day}\right)(\cancel{9.101\times10^{-6}\ M})\ 6.25\times10^{-5}}$$

~~$t_{char} = 179.115$ days~~

$\boxed{t_{char} = 26.07\ days}$

(iii) characteristic rxn time according to second definition (n=2)

$$t_{char} = \frac{1}{k_2 C_B(0)} = \frac{1}{\left(1054.08\frac{1}{M\cdot days}\right)(\cancel{9.101\times10^{-6}}\ M)\ 6.25\times10^{-5}}$$

~~$t_{char} = 104.24$ days~~

$\boxed{t_{char} = 15.18\ days}$

b) if C_{O_2} is in great excess then $r_{Mn^{2+}}$ can be treated as psuedo-first order where

$k^* = kC_{O_2} = \left(1054.08\frac{1}{M\cdot day}\right)(6.25\times10^{-5}\ M) = 0.066\frac{1}{days}$

$\cancel{V}\frac{dC_{Mn^{2+}}}{dt} = \cancel{V}r_{Mn^{2+}} = -k^* C_{Mn^{2+}}$

$\int_{C_{Mn,0}}^{C_{Mn,t}} \frac{dC_{Mn^{2+}}}{C_{Mn^{2+}}} = \int_0^t -k^* dt$

$\ln(C_{Mn^{2+}})(t) - \ln(C_{Mn^{2+}})(0) = -k^*t \Rightarrow C_{Mn^{2+}}(t) = C_{Mn^{2+}}(0)\exp(-kt)$

$$\frac{\ln\left(\frac{C_{Mn^{2+}}(t)}{C_{Mn^{2+}}(0)}\right)}{-k^*} = t$$

Find t where $C_{Mn^{2+}}(t) = 20\ \mu g/L\left(\frac{1\ g}{1\times10^6\ \mu g}\right)\left(\frac{1\ mol}{54.938\ g}\right) = 3.64\times10^{-7}\ M$

$$t = \frac{\ln\left(\frac{3.64\times10^{-7}\ M}{9.101\times10^{-6}\ M}\right)}{-0.066\frac{1}{days}}\ \boxed{= 48.77\ days}$$ → slightly shorter time than second-order rxn

t-char by def #1:

$t_{char} = k^{*-1} = \left(0.066\frac{1}{days}\right)^{-1}$

$\boxed{= 15.15\ days}$

tchar by def #2:

$t_{char} = k^{*-1}$

$\boxed{= 15.15\ days}$

```r
#==============================================================================
# graph for hw 2 problem 4
#
# Tyler Bradley
# 1/28/2018
#==============================================================================

# loading required libraries
library(tidyverse)
library(knitr)
library(kableExtra)
```

Part a Defining constants

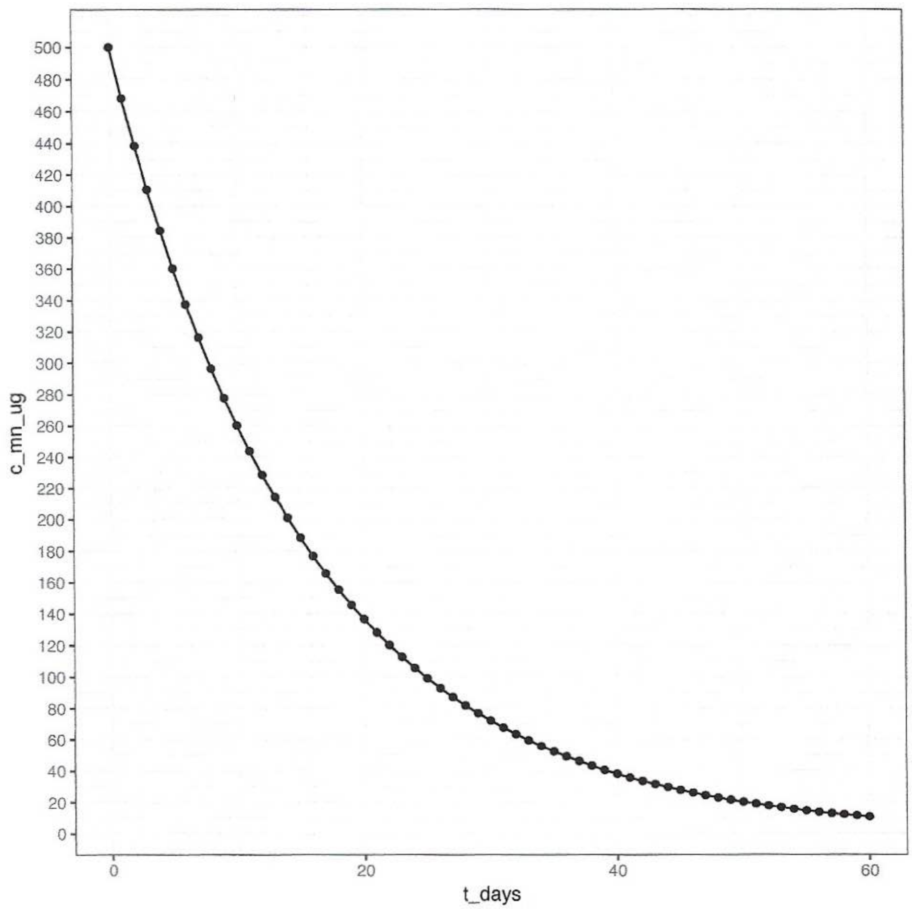
```r
a <- 4
b <- 1
k <- 1054.08 # [=] £M^{-1} * days^{-1}£
cb_o = 6.25e-5 # [=] M
ca_o = 9.101e-6 # [=] M
```

Creating data set C_{Mn} is calculated from formula derived in problem

```r
mn_data <- tibble(t_days = seq(0, 60, by = 1)) %>%
  mutate(c_mn_mol = ((ca_o - (a / b) * cb_o) / (
    1 - (a / b) * (cb_o / ca_o) * exp(-(((
      b * ca_o
    ) / (
      a * cb_o
    )) - 1) * cb_o * k * t_days)
  )),
  c_mn_ug = c_mn_mol * 54.938 * 1e6)
```

Plotting the decay equation

```r
ggplot(mn_data, aes(t_days, c_mn_ug)) +
  geom_point() +
  geom_line() +
  theme_bw() +
  scale_y_continuous(breaks = seq(0, 500, by = 20))
```



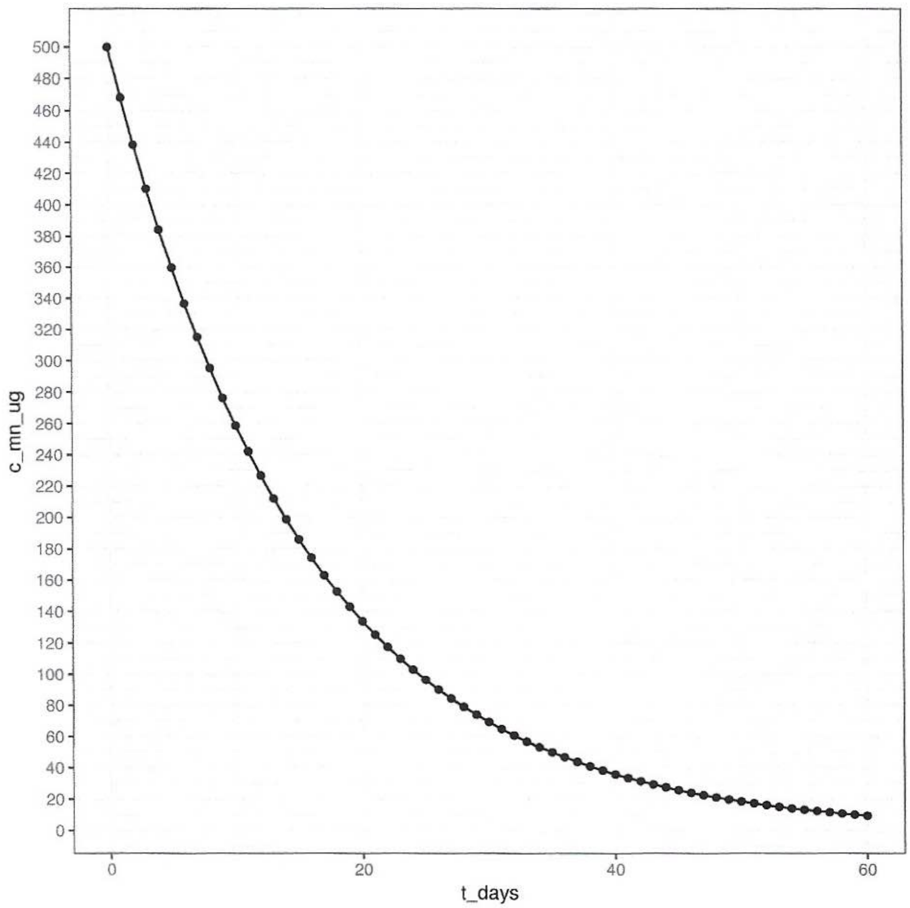
Part b CO_2 is in great excess so r_{mn} becomes a psuedo-first order equation

```
k_star <- k * cb_o

mn_data_b <- tibble(t_days = seq(0, 60, by = 1)) %>%
  mutate(c_mn_mol = ca_o * exp(-k_star*t_days),
         c_mn_ug = c_mn_mol * 54.938 * 1e6)
```

Plotting decay rxn as psuedo-first order

```
ggplot(mn_data_b, aes(t_days, c_mn_ug)) +
  geom_point() +
  geom_line() +
  theme_bw() +
  scale_y_continuous(breaks = seq(0, 500, by = 20))
```



c_mn_ug
t_days
0
20
40
60
500
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0

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(3) $NH_2Cl + DMA \longrightarrow UDMH$

$k = 0.081 \frac{1}{M \cdot s}$

$C_A(0) = C_B(0) = 1 \times 10^{-3}\ M$

a) $t_{char} = \frac{1}{k\, C_A(0)}$

$= \frac{1}{(0.081 \frac{1}{\cancel{M} \cdot s})(1 \times 10^{-3}\ \cancel{M})}$

$\boxed{t_{char} = 1.23 \times 10^{4}\ s}$

b) $C_A(0) = C_B(0) = 3 \times 10^{-5}\ M$

$t_{char} = \frac{1}{(0.081 \frac{1}{M \cdot s})(3 \times 10^{-5}\ M)}$

$\boxed{t_{char} = 4.12 \times 10^{5}\ s}$

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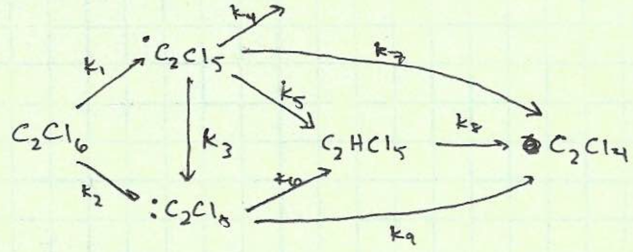

a) write rxn rate expressions for C_2Cl_6, $\cdot C_2Cl_5$, $:C_2Cl_5$, C_2HCl_5, and C_2Cl_4

$$\frac{d[C_2Cl_6]}{dt} = -k_1[C_2Cl_6] - k_2[C_2Cl_6]$$

$$\frac{d[\cdot C_2Cl_5]}{dt} = k_1[C_2Cl_6] - (k_3 + k_4 + k_5)[\cdot C_2Cl_5] - k_7[\cdot C_2Cl_5]$$

$$\frac{d[:C_2Cl_5]}{dt} = k_2[C_2Cl_6] + k_3[C_2Cl_5] - (k_6 + k_9)[:C_2Cl_5]$$

$$\frac{d[C_2HCl_5]}{dt} = k_6[:C_2Cl_5] + k_5[\cdot C_2Cl_5] - k_8[C_2HCl_5]$$

$$\frac{d[C_2Cl_4]}{dt} = k_7[\cdot C_2Cl_5] + k_8[C_2HCl_5] + k_9[:C_2Cl_5]$$

b) k_1, k_5, and k_8 are major rxn pathways → write rxn rate exp. for all compounds involved

$$\frac{d[C_2Cl_6]}{dt} = -k_1[C_2Cl_6]$$

$$\frac{d[\cdot C_2Cl_5]}{dt} = k_1[C_2Cl_6] - k_5[\cdot C_2Cl_5]$$

$$\frac{d[C_2HCl_5]}{dt} = k_5[\cdot C_2Cl_5] - k_8[C_2HCl_5]$$

$$\frac{d[C_2Cl_4]}{dt} = k_8[C_2HCl_5]$$

c) if $k_5 >> k_1$ show that $\cdot C_2Cl_5$ can be removed from pathway:

↳ As soon as C_2Cl_6 is available it will be converted to $\cdot C_2Cl_5$, since k_5 is significantly larger than k_1, as soon as the $\cdot C_2Cl_5$ is available it will be consumed and converted to $[C_2HCl_2]$ so $\frac{d[\cdot C_2Cl_5]}{dt}$ will be negligible and can be set to zero.

$$\frac{d[\cdot C_2Cl_5]}{dt} = 0 = k_1[C_2Cl_6] - k_5[\cdot C_2Cl_5]$$

$$k_1[C_2Cl_6] = k_5[\cdot C_2Cl_5]$$

↳ Because of this, $[\cdot C_2Cl_5]$ can be substituted out of the $\frac{d[C_2HCl_5]}{dt}$ equation and the overall rxn can be simplified