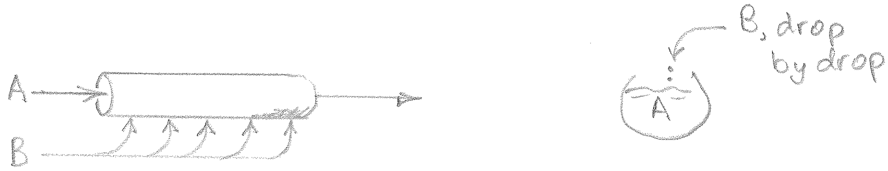
8.1

a) $r_1 = k_1 C_A C_B^2$

$r_2 = k_2 C_R C_B$

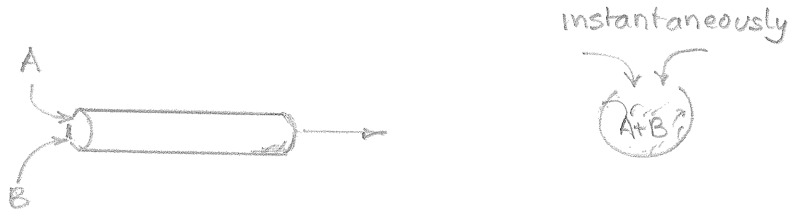
b) $r_1 = k_1 C_A C_B$

$r_2 = k_2 C_R C_B^2$



c) $r_1 = k_1 C_A C_B$

$r_2 = k_2 C_R^2 C_B$



d) $r_1 = k_1 C_A^2 C_B$

$r_2 = k_2 C_R C_B$

8.3 Guess $A \to R \to S$. Now check Fig 14. This shows that the results don't fit these kinetics

Next guess $A \nearrow R$, $\searrow S$ $\cdots$ $r_R = k_1 C_A$, $r_S = k_2 C_A$ } Then for mixed flow

$$\left.\begin{aligned} \tau &= \frac{C_R - C_{R0}}{k_1 C_A} \\ \tau &= \frac{C_S - C_{S0}}{k_2 C_A} \end{aligned}\right\} \text{ dividing gives } \quad \frac{C_R}{C_S} = \frac{k_1}{k_2} = \text{constant}$$

This agrees with the observed so we conclude that

$$\left.\begin{aligned} A &\nearrow R \;\cdots\; r_R = k_1 C_A \\ A &\searrow S \;\cdots\; r_S = k_2 C_A \end{aligned}\right\} \quad k_1 = 1.5\, k_2 \longleftarrow$$

8.5 Guess $A \to R \to S$. Then check Fig 14. This shows that our guess was correct and that

$$\frac{k_2}{k_1} = 0.25$$

8.5 (continued)

Let us next evaluate the rate constants

For run 1 $\tau_1 = \frac{C_{A0}-C_A}{k_1 C_A} = \frac{100-50}{50k_1}$ $\therefore k_1 = \frac{1}{\tau_1} = \frac{1}{5} = 0.2\ \text{min}^{-1}$

For run 2 $\tau_2 = \frac{100-20}{k_1 20} = \frac{4}{k_1}$ $\therefore k_1 = \frac{4}{\tau_2} = \frac{4}{20} = 0.2\ \text{min}^{-1}$

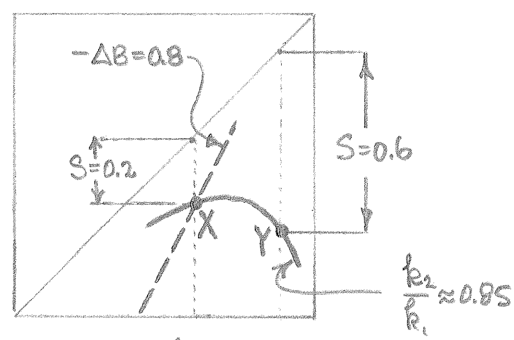
these results are consistent

Therefore the kinetics are

$$A \xrightarrow[n_1=1]{k_1=0.2\,\text{min}^{-1}} R \xrightarrow[n_2=1]{k_2=0.05\,\text{min}^{-1}} S$$

8.7 a) At the start $\begin{cases} A_0 = 1 \\ B_0 = 3 \end{cases}$

After some time $\begin{cases} B = 2.2 \\ S = 0.2 \end{cases}$



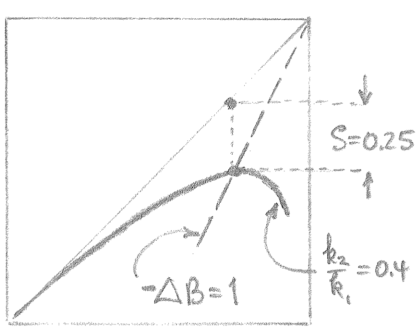
By material balance $-\Delta B = 0.8$, and using ΔB & S locates point X on Fig. 7.15.

At this point $k_2/k_1 = 0.85$

Following this k_2/k_1 line to $S = 0.6$ (point Y) gives $\begin{cases} A = 0.1 \\ R = 0.3 \\ S = 0.6 \\ B = 3-2(0.6)-0.3 = 1.5 \end{cases}$ ← a)

b) Nothing ← b)

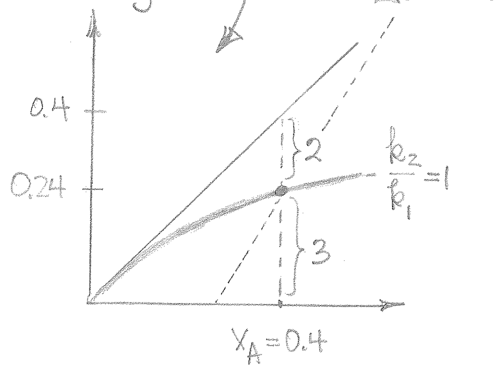
c)



Since the reaction is rapid the R actually formed is probably less than what could be formed. Thus the observed k ratio, $k_2/k_1 = 0.4$ from Fig 7.15 is the upper bound to the true k ratio.

$\therefore k_2/k_1 \leq 0.4$ ← c)

8.9 From Fig. 14



Thus

given → $\frac{C_A}{C_{A0}} = 0.6$

$$\left.\begin{aligned}\frac{C_R}{C_{A0}} &= 0.24\\ \frac{C_S}{C_{A0}} &= 0.16\\ \frac{C_B}{C_{A0}} &= 0.42\end{aligned}\right\} \frac{k_2}{k_1} = 1 \longleftarrow$$

8.11 Evaluate k_1 and k_2 at various pH.

pH	k_1	k_2
2	3	11
4	5	7
6	7	11

from this table:

Operate at pH = 6 because it gives the highest k_1 and the highest k_2 ←

8.13 Assume that $C_{A0}=100$. Then

a) If you have produced lots of S & U, and if the second step reactions are relatively very slow, then the first step reactions are complete. So

$C_A=0 \quad C_R=20 \quad C_S=20 \quad C_T=20$ and $C_U=40$ ← a)

b) The second step reactions are very fast, so any R formed has transformed into S and U. So $C_{R\,formed} = 20+40=60$

Thus $C_T = \frac{1}{2} C_{R\,formed} = 30$. So

$C_A=10 \quad C_R=0 \quad C_S=20 \quad C_T=30$ and $C_U=40$ ← b)

8.15 Our reaction scheme is

$$A \xrightarrow[\text{①}]{\text{medium}} R \xrightarrow[\text{③}]{\text{fast}} S, \qquad A \xrightarrow[\text{② rate}]{\text{medium}} S \xrightarrow[\text{④}]{\text{slow}} T$$

Combining gives

$$\frac{1}{k_{13}} = \frac{1}{k_1} + \frac{1}{k_3} = \frac{1}{0.21} + \frac{1}{4.2} = \frac{1}{0.2}$$

$$A \xrightarrow{0.2} S \xrightarrow{0.004} T, \qquad A \xrightarrow{0.2} S$$

thus

$$A \xrightarrow[k_{123}]{0.4} S \xrightarrow[k_4]{0.004} T \quad \cdots \text{ or } \quad \frac{k_{123}}{k_4} = 100$$

Since S is desired use plug flow. Then an extension of Eq. 49 gives

$$\frac{C_{S\,max}}{C_{A0}} = \left(\frac{k_{123}}{k_4}\right)^{k_4/(k_4-k_{123})} = \left(\frac{0.4}{0.004}\right)^{0.004/(0.004-0.4)}$$

$$= 0.955 \quad \cdots \text{ or } \quad C_{S\,max} = 0.955\, C_{A0} \longleftarrow$$

8.17 Since this is a course on chemical reactors let us make the analogy of this process to a chemical process, so

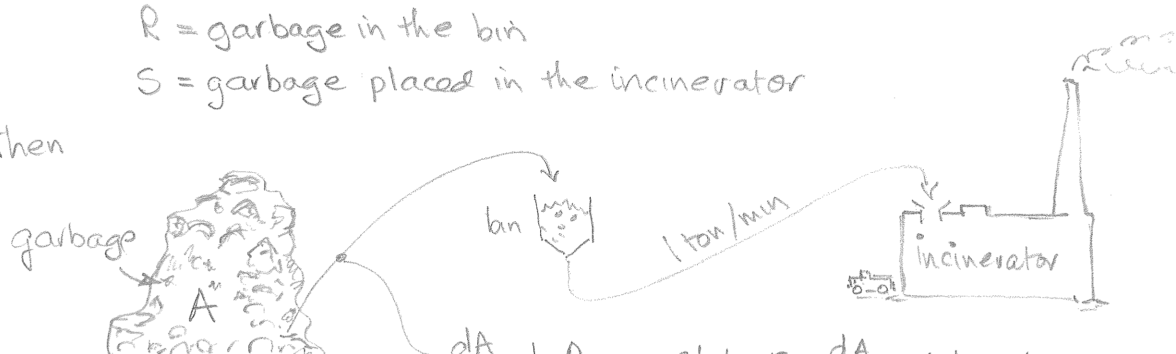
Let A = garbage still to be collected

$A_0 = 1440$ tons

R = garbage in the bin

S = garbage placed in the incinerator

Then



$$\frac{dA}{dt} = k_1 A \quad \cdots \quad \text{at } t=0 \quad -\frac{dA_0}{dt} = 6 \text{ tons/min}$$

$$\therefore \quad k_1 = \frac{-dA/dt}{A} = \frac{6}{1440} = \frac{1}{240} \text{ min}^{-1}$$

Then

$$A \xrightarrow[k_1 = \frac{1}{240} \text{ min}^{-1}]{n_1 = 1} R \xrightarrow[k_2 = 1 \text{ ton/min}]{n_2 = 0} S$$

with

$$-\frac{dA}{dt} = k_1 A \quad \text{and} \quad \frac{dR}{dt} = k_1 A - k_2 \quad \cdots\cdots\cdots \text{(i)}$$

8.17 (continued)

Integrating Eq (i) gives (see Eqs 18 and 19 in the text)

$$A = A_0 e^{-k_1 t} = 1440 e^{-t/240} \quad \cdots\cdots \quad (ii)$$

$$R = A_0(1-e^{-k_1 t}) - k_2 t = 1440(1-e^{-t/240}) - t \quad \cdots (iii)$$

(a) 95% collected. From Eq (ii)

$$\frac{A}{A_0} = \frac{1}{20} = e^{-t/240}$$

or

$$t = 240 \ln 20 = 720 \text{ min} = 12 \text{ hr}$$

∴ at 6pm 95% of the days garbage will have been collected ——— a)

(c) Time when bin is full. This will occur where $dR/dt = 0$. So from Eq.(i)

$$\frac{dR}{dt} = 0 = k_1 A - k_2 \quad \cdots \text{ or } \quad A = \frac{k_2}{k_1} = \frac{1}{1/240} = 240 \text{ tons}$$

The time, from Eq. (ii)

$$240 = 1440 e^{-t/240} \quad \cdots \text{ or } \quad t = 240 \ln 6 = 430 \text{ min}$$

or 1.20 pm ——— c)

(b) Max contents of the bin

$$R_{max} = 1440(1-e^{-430/240}) - 430 \quad \cdots \text{ or } \quad R_{max} = 430 \text{ tons}$$ ——— b)

(d) The bin empties when R=0. Again look at Eq (iii)

$$R = 0 = 1440(1-e^{-t/240}) - t$$

or

$$e^{-t/240} + t = 1$$

Solve by trial & error

$$t = 1436 \text{ min} = 23 \text{ hr } 56 \text{ min}$$

5.56 am ——— d)

What this means that the incinerator works full time, the whole operation proceeds continuously -- It is well designed, but with nothing to spare

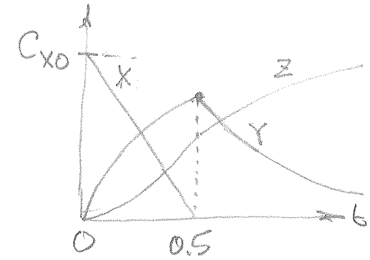
8.19 Let us follow the text. From Eq 22

$$X \xrightarrow{n_1=0} Y \xrightarrow[k_2=1.5\,hr^{-1}]{n_2=1} Z \qquad C_{X0} = 100\ mol/m^3$$

we are given

$$k_1 = \frac{100\,mol/m^3}{1/2\,hr} = 200\ mol/m^3\cdot hr$$

$$\therefore K = \frac{k_2 C_{X0}}{k_1} = \frac{(1.5)(100)}{200} = 0.75$$



(a) at half an hour one gets Y_{max} (see Fig 8.8)

$$\frac{C_{Y\,max}}{C_{X0}} = \frac{1}{K}\left(1-e^{-K}\right) = \frac{1}{0.75}\left(1-e^{-0.75}\right) = 0.7035 \longleftarrow a)$$

(b) After one hour note that X is all gone and we only have Y & Z present

$$\frac{C_Y}{C_{X0}} = \frac{1}{K}\left(e^{+K-k_2 t} - e^{-k_2 t}\right)$$

$$= \frac{1}{0.75}\left(e^{-0.75-1.5} - e^{-1.5}\right) = 0.3323$$

$$\therefore \frac{C_Z}{C_{X0}} = 1 - 0.3323 = 0.6677 \longleftarrow b)$$

8.21 The reaction is $A \xrightarrow{6} R \begin{smallmatrix} \xrightarrow{3} S \\ \xrightarrow{1} T \end{smallmatrix}$ for which from Eq 49

$$\left(\frac{C_R}{C_{A0}}\right)_{max} = \left(\frac{k_1}{k_{34}}\right)^{k_{34}/(k_{34}-k_1)} = \left(\frac{6}{4}\right)^{4/4-6} = 0.444$$

or $C_{Rmax} = 0.444\ mol/lit \longleftarrow$

From Eq. 50

$$t_{R,max} = \frac{\ln(k_{34}/k_1)}{k_{34}-k_1} = \frac{\ln 4/6}{4-6} = 0.2027\,h = 12.2\ min \longleftarrow$$

Alternatively, from Fig. 13, for $\frac{k_{34}}{k_1} = \frac{2}{3}$ ... we find $\left(\frac{C_R}{C_{A0}}\right)_{max} = 0.44 \longleftarrow$
