

1. Addition of alum to drinking water

(a) Estimate/calculate concentration of  $\text{Al}^{3+}$



$$\frac{\{\text{Al}^{3+}\}\{\text{OH}^-\}^3}{\{\text{Al}(\text{OH})_3(s)\}} = 6.3 \times 10^{-32} \Rightarrow [\text{Al}^{3+}][\text{OH}^-]^3 = 6.3 \times 10^{-32}$$

$$\text{Given } \text{pH} = 5.8 \Rightarrow [\text{H}^+] = 10^{-5.8} = 1.585 \times 10^{-6} \text{ M}$$

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \Rightarrow [\text{OH}^-] = 6.31 \times 10^{-9} \text{ M}$$

$$[\text{Al}^{3+}][6.31 \times 10^{-9}]^3 = 6.3 \times 10^{-32}$$

$$[\text{Al}^{3+}] = 2.51 \times 10^{-7} \text{ mol/L} \quad \dots \text{ now convert to mg/L}$$

$$[\text{Al}^{3+}] = 2.51 \times 10^{-7} \frac{\text{mol}}{\text{L}} \times \frac{26.98 \text{ g}}{\text{mole}} \times \frac{1000 \text{ mg}}{\text{g}}$$

$$\boxed{[\text{Al}^{3+}] = 0.0068 \text{ mg/L}}$$

(b) Is it a problem to meet the standard?

It looks like no problem. We can have up to 0.1 mg/L of  $\text{Al}^{3+}$  and we have only 0.0068 mg/L. We are pretty far below the secondary standard. I see no cause for worry.

## 2. Conversion of Chemical X

(a) What is the reaction order?

$t$ (min)	$C$ (mmol/L)	$\ln C$	$1/C$ (L/mmol)
5	1.6	0.470	0.625
10	0.80	-0.223	1.25
15	0.40	-0.916	2.50
20	0.20	-1.61	5.00
25	0.10	-2.30	10.0

clearly not linear in time

looks linear!

clearly not linear in time

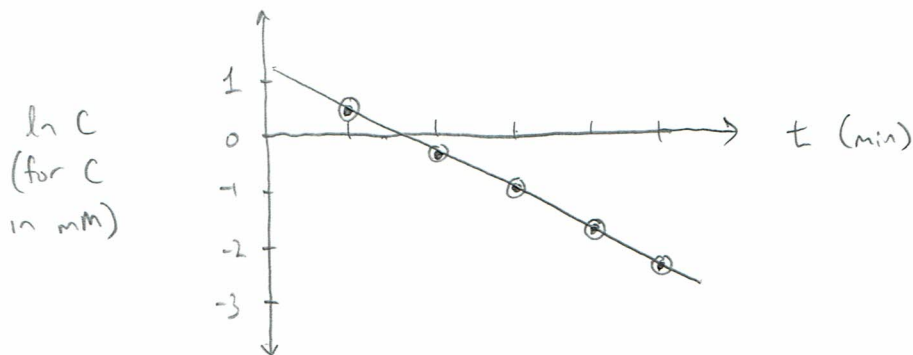
Because  $\ln(C)$  is linear in time, it must be first-order kinetics

(b) Estimate/calculate the rate coefficient

First-order kinetics in a batch reactor:  $C = C_0 e^{-kt}$

$$\ln C = \ln C_0 - kt$$

Graph  $\ln C$  vs  $t$ , find the slope, slope =  $-k$



$$\text{slope} = \frac{\Delta[\ln C]}{\Delta t} \quad \dots \text{choose any two points}$$

$$\text{slope} = \frac{-2.30 - 0.470}{25 \text{ min} - 5 \text{ min}} = \frac{-2.77}{20 \text{ min}} = -0.1385 \text{ min}^{-1} \Rightarrow$$

$$k_1 = 0.14 \text{ min}^{-1}$$

2. continued

© CMFR or PFR?

We don't know a lot of details, so maybe we can't say for sure which reactor is "better" in this case. But in general, choose the PFR for first-order reactions because it is more efficient.

You can get more conversion in a PFR than in a CMFR if they have the same  $k_1$  and the same residence time. Since we want to remove a toxic chemical, let's pick the PFR so we can get rid of it more efficiently.

④ Specify the volume of reactor

PFR, steady-state, first-order:  $C_E = C_I e^{-k_1 \theta}$

Given  $C_I = 1.0 \text{ mM}$ ,  $C_E = 0.05 \text{ mM}$ , and know  $k_1 = 0.14 \text{ min}^{-1}$

$$(0.05 \text{ mM}) = (1.0 \text{ mM}) \cdot \exp[-(0.139 \text{ min}^{-1}) \theta]$$

$$\text{solve} \Rightarrow \theta = 21.55 \text{ min} = 0.3592 \text{ hr}$$

Given  $Q = 25 \text{ m}^3/\text{hr}$  and we know  $\theta = V/Q \Rightarrow V = \theta Q$

$$V = (0.3592 \text{ hr})(25 \text{ m}^3/\text{hr}) \Rightarrow \boxed{V \geq 9.0 \text{ m}^3} \text{ to get the desired conversion.}$$

If you said CMFR:  $C_E = C_I \left( \frac{1}{1+k_1 \theta} \right)$  for CMFR, 1<sup>st</sup>-order, steady state

$$0.05 \text{ mM} = (1.0 \text{ mM}) \left( \frac{1}{1+k_1 \theta} \right) \Rightarrow k_1 \theta = 19 \Rightarrow \theta = \frac{19}{k_1}$$

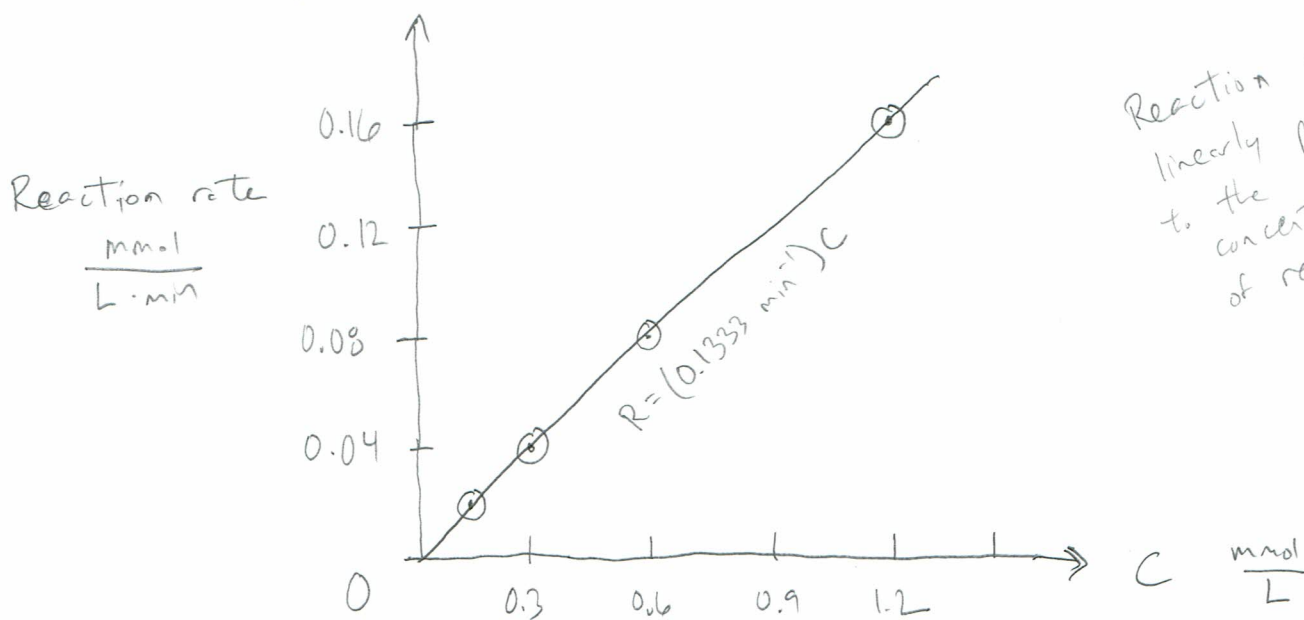
$$\theta = \frac{19}{0.139 \text{ min}^{-1}} = 137 \text{ min} = 2.28 \text{ hr}$$

$$V = Q \theta = (25 \text{ m}^3/\text{hr})(2.28 \text{ hr}) = \boxed{57 \text{ m}^3} \dots \text{much higher volume required for CMFR than for PFR}$$

Alternate method for problem 2(a), 2(b)

$t$ (min)	$C$ (mmol/L)	Average $C$ in time interval	Reaction rate $\frac{\Delta C}{\Delta t}$ mmol/(L·min)
5	1.6	1.2 $\frac{\text{mmol}}{\text{L}}$	$\frac{1.6-0.8}{10-5} = 0.16$
10	0.8		0.6
15	0.4	0.3	
20	0.2		0.15
25	0.1		

Now graph  $R$  vs  $C$  ... four data points



(a) Reaction rate is linearly proportional to concentration of reactant!  
So it's first-order.

(b)  $R = k_1 C$  ... what is the slope of the graph?  $0.1333 \text{ min}^{-1}$

$k_1 = 0.13 \text{ min}^{-1}$  ... actually the correct value is closer to  $0.14 \text{ min}^{-1}$ , there is a little error introduced by calculating  $\Delta C/\Delta t$ . But it's close enough!

### 3. BOD in a sample of river water

#### (a) Estimate/calculate $L_0$

The trick here is to notice that the concentration of dissolved oxygen is clearly approaching a steady level of  $2.10 \text{ mg/L}$ .

You can see this if you look at the data from  $t=8 \text{ d}$ ,  $9 \text{ d}$ ,  $10 \text{ d}$ .

$$\text{Thus: } \text{BOD}_{\text{ult}} = 8.90 \text{ mg/L} - 2.10 \text{ mg/L} = 6.80 \text{ mg/L}$$

$$\text{But } L_0 = \text{BOD}_{\text{ult}}!$$

Thus  $L_0 = 6.80 \text{ mg/L}$  initial concentration of contaminant, expressed as oxygen demand

#### (b) Estimate/calculate time from sample #2

$$\text{BOD}_t = 8.90 \text{ mg/L} - 4.0 \text{ mg/L} = 4.90 \text{ mg/L}$$

$$\text{BOD}_t = \text{BOD}_{\text{ult}} \{ 1 - \exp[-k, t] \}$$

$$(4.90 \text{ mg/L}) = (6.80 \text{ mg/L}) \{ 1 - \exp[-(0.80 \text{ d}^{-1}) t] \}$$

$$\text{solving, } t = 1.6 \text{ d}$$

#### (c) Estimate/calculate time for sample #3

Same procedure as part (b).

$$\text{BOD}_t = 8.90 \text{ mg/L} - 2.5 \text{ mg/L} = 6.40 \text{ mg/L}$$

$$\text{BOD}_t = \text{BOD}_{\text{ult}} \{ 1 - \exp[-k, t] \}$$

$$6.40 \text{ mg/L} = (6.80 \text{ mg/L}) \{ 1 - \exp[-(0.80 \text{ d}^{-1}) t] \}$$

$$\text{solving, } t = 3.5 \text{ d} \dots \text{OK if you got } t=3.6 \text{ d} \dots \text{rounding error}$$