

## ESE5001 Environmental Engineering Principles Chemical Principles Practice Questions

### 1. Units and unit conversion exercises

- (a) Vinyl chloride ( $C_2H_3Cl$ ) is a confirmed carcinogen that is sometimes found in drinking water. If it is present in drinking water at a level of 80 ppb, what is the mass concentration of vinyl chloride in water (in  $\mu g/L$ )?
- (b) The maximum contaminant level for cadmium in drinking water is 0.005 mg/L. Convert this mass concentration into a mass fraction in units of parts per million (ppm).
- (c) A brochure from a municipal water supply agency lists the following average concentrations of selected ions in drinking water:

|           |                  |
|-----------|------------------|
| $Fe^{3+}$ | 0.02 mg $L^{-1}$ |
| $Ca^{2+}$ | 9.8 mg $L^{-1}$  |
| $Mg^{2+}$ | 1.8 mg $L^{-1}$  |
| $K^{+}$   | 0.6 mg $L^{-1}$  |
| $Na^{+}$  | 4.6 mg $L^{-1}$  |

Compute the molarity and normality of each of these species.

### 2. River Water Quality

Given the characteristics listed below for a “typical” river, determine the following parameters related to drinking water quality. The water temperature is 25°C.

- (a) Total hardness (meq/L)
- (b) Carbonate hardness (meq/L)
- (c) Noncarbonate hardness (meq/L)
- (d) Total dissolved solids (mg/L)
- (e) Alkalinity (meq/L)
- (f) Ionic Strength (M)
- (g) pH
- (h) Check the electroneutrality balance.

| Species     | Concentration (mg/L) | Species     | Concentration (mg/L) |
|-------------|----------------------|-------------|----------------------|
| $Ca^{2+}$   | 15                   | $CO_3^{2-}$ | 0.0085               |
| $Mg^{2+}$   | 4.1                  | $SO_4^{2-}$ | 11.2                 |
| $Na^{+}$    | 6.3                  | $Cl^{-}$    | 7.8                  |
| $K^{+}$     | 2.3                  | $NO_3^{-}$  | 1                    |
| $H^{+}$     | 0.32 ( $\mu g/L$ )   | $SiO_2$     | 13.1                 |
| $HCO_3^{-}$ | 58.4                 |             |                      |

### 3. Nitrogen dissolved in water

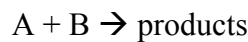
- (a) Determine the mass concentration of  $N_2$  in water at 20 °C when the water is in equilibrium with the atmosphere.
- (b) Compare your result with the equilibrium mass concentration of  $O_2$  in water exposed to the atmosphere: 9.1 mg/L at 20 °C. Explain.

#### 4. Window cleaner chemistry

One of the active ingredients in window cleaner is ammonium hydroxide ( $\text{NH}_4\text{OH}$ ). Consider the following situation:  $10^{-3}$  moles of ammonium hydroxide is added to pure water to form 1 L of solution. The solution is placed into a 1 L glass jar and sealed (without any air space). The ammonium hydroxide fully dissolves to  $\text{NH}_4^+$  and  $\text{OH}^-$ . The liberated ammonium ion is weak acid ( $\text{pK}_\text{A} = 9.23$ ). Determine the equilibrium pH of the liquid.

#### 5. Elementary reaction kinetics

- A species in a batch reactor undergoes first-order decay with a rate constant of  $0.3 \text{ h}^{-1}$ . How much time must pass before the species concentration is reduced to 10% of its initial value?
- A species undergoes first-order decay in a batch reactor. Three hours after the reactor is sealed, the species concentration is 20% of its initial value. What is the rate constant?
- Two reactants, A and B, are placed in a batch reactor where they undergo the following elementary reaction:

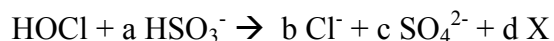


The initial concentrations are  $[\text{A}] = 0.1 \text{ M}$  and  $[\text{B}] = 0.001 \text{ M}$ . The reaction rate constant is  $3 \text{ M}^{-1} \text{ h}^{-1}$ . What are the steady-state concentrations of  $[\text{A}]$  and  $[\text{B}]$ ?

- For the conditions in part (c), what is the characteristic time to achieve steady-state in the reactor?

#### 6. Redox stoichiometry

Often, wastewater is disinfected with hypochlorous ( $\text{HOCl}$ ) before discharging it to the environment. To avoid damaging the receiving waters, the disinfection step is often followed by a “dechlorination” step: bisulfate ( $\text{HSO}_3^-$ ) is added to the water to react with excess hypochlorous acid. The overall reaction is



where the letters a – d represent stoichiometric coefficients and the symbol X represents a chemical element or compound.

- Give the oxidation states of the following elements: Cl in  $\text{HOCl}$ ; Cl in  $\text{Cl}^-$ ; S in  $\text{HSO}_3^-$ ; S in  $\text{SO}_4^{2-}$ .
- Determine the stoichiometric coefficients, a – c.
- What is the unknown species, X and its stoichiometric coefficient d?

#### 7. Biochemical Oxygen Demand

An experiment was conducted in a batch reactor to measure the BOD in a water sample. The water sample was placed in a reactor and the dissolved oxygen

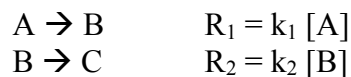
content (DO) was measured as a function of time. The measurement data are presented below. Use these data to answer the following questions.

| Time     | DO (mg/L) |
|----------|-----------|
| 0        | 10        |
| 1        | 8.7       |
| 2        | 7.6       |
| 3        | 6.8       |
| 4        | 6.2       |
| 5        | 5.7       |
| 6        | 5.3       |
| 7        | 5.0       |
| 8        | 4.8       |
| 9        | 4.6       |
| 10       | 4.5       |
| 15       | 4.1       |
| $\infty$ | 4.0       |

- What is the ultimate BOD of the sample ( $BOD_u$ )?
- What is the 5-day BOD of the sample ( $BOD_5$ )?
- What is the reaction rate constant,  $k$ , for BOD degradation?

### 8. Batch reactor kinetics: Sequential first-order reactions

A batch reactor is initially filled with water that contains species A at concentration  $A_0$ . Except for this species, the water is pure. After the reactor is sealed, the following chemical reactions occur:



- Derive an explicit equation that yields the concentration of species A as a function of time.
- Fluid is kept in the batch reactor for a time period  $T$ . Write a mathematical condition for  $T$  that, if satisfied, would permit the approximation  $[A](T) \approx A_0$ . [Hint:  $T = 0$  is unnecessarily restrictive.]

Assume for the remainder of the problem that  $[A](T) \approx A_0$ . Also assume that the reaction rate constants satisfy the condition  $k_1 \ll k_2$ . (3 marks)

- Write a governing equation that describes the rate of change of  $[B]$ .
- Derive an explicit expression for the steady-state concentration of  $[B]$ .
- What is the characteristic time required for the steady-state solution in (d) to be attained?
- Derive an explicit equation for the time-dependent concentration of  $[B]$ .

## SOLUTIONS

### 1. Units and unit conversion exercises

1a) Mass Concentration of  $C_2H_3Cl$  in  $H_2O$   

$$= \left( \frac{80 \times 10^{-9} \text{ g } C_2H_3Cl}{\text{g } H_2O} \right) \left( \frac{10^6 \mu\text{g}}{\text{g}} \right) \left( \frac{10^3 \text{ g}}{\text{kg}} \right) \left( \frac{1 \text{ kg } H_2O}{\text{L } H_2O} \right)$$

$$= \boxed{80 \mu\text{g/L}}$$
 Note: In general,  $[ppb] = [\mu\text{g/L}]$  in  $H_2O$

1b) Mass Fraction  

$$= \left( \frac{0.005 \text{ mg Cd}}{\text{L } H_2O} \right) \left( \frac{1 \text{ L } H_2O}{1000 \text{ g } H_2O} \right) \left( \frac{1 \text{ g Cd}}{10^3 \text{ mg Cd}} \right) (10^6)$$

1c) =  $\boxed{0.005 \text{ ppm}}$

| Species   | Mass conc (mg/L) | MW | Net charge | $M$ (Mol/L)          | $N$ (eq/L)           |
|-----------|------------------|----|------------|----------------------|----------------------|
| $Fe^{3+}$ | 0.02             | 56 | 3          | $3.6 \times 10^{-7}$ | $1.1 \times 10^{-6}$ |
| $Ca^{2+}$ | 9.8              | 40 | 2          | $2.5 \times 10^{-4}$ | $4.9 \times 10^{-4}$ |
| $Mg^{2+}$ | 1.8              | 24 | 2          | $7.5 \times 10^{-5}$ | $1.5 \times 10^{-4}$ |
| $K^+$     | 0.6              | 39 | 1          | $1.5 \times 10^{-5}$ | $1.5 \times 10^{-5}$ |
| $Na^+$    | 4.6              | 23 | 1          | $2.0 \times 10^{-4}$ | $2.0 \times 10^{-4}$ |

to convert to M ppm N

### 2. River Water Quality

- (a) Total hardness is defined as the sum of the normalities of multivalent cations. The multivalent cations present in the river water are  $Ca^{2+}$  and  $Mg^{2+}$ . The hardness is calculated as follows:

| Species   | Mass Concentration [mg L <sup>-1</sup> ] | MW <sub>i</sub> [g mol <sup>-1</sup> ] | $M_i$ [mol L <sup>-1</sup> ] | $N_i$ [eq L <sup>-1</sup> ] |
|-----------|--|--|------------------------------|-----------------------------|
| $Ca^{2+}$ | 15                                       | 40                                     | $3.75 \times 10^{-4}$        | $7.5 \times 10^{-4}$        |
| $Mg^{2+}$ | 4.1                                      | 24                                     | $1.71 \times 10^{-4}$        | $3.42 \times 10^{-4}$       |

$$\Sigma = 1.1 \times 10^{-3}$$

Therefore the total hardness is:

$$\boxed{TH = 1.1 \text{ meq L}^{-1}}$$

- (b) Carbonate hardness (CH) is found by summing the normalities of  $CO_3^{2-}$  and  $HCO_3^-$ . If this sum is less than TH then CH is set equal to this sum. If this sum is greater than TH, then CH = TH. In this case, the normalities of the carbonate species are as follows:

$$\left( \frac{0.0085 \text{ mg}}{\text{L}} \right) \left( \frac{1 \text{ mmol}}{60 \text{ mg}} \right) (2) + \left( \frac{58.4 \text{ mg}}{\text{L}} \right) \left( \frac{1 \text{ mmol}}{61 \text{ mg}} \right) (1)$$

$$= 0.96 \text{ meq L}^{-1}$$

Since this value is less than TH,  $\boxed{CH = 0.96 \text{ meq L}^{-1}}$

- (d) We can assume that none of the components listed are filterable (although  $SiO_2$  may be in the form of filterable particles, this is neglected here). Thus, TDS is found by:

$$TDS = [15 + 4.1 + 6.3 + 2.3 + 0.67 + 0.32 \times 10^{-3} + 58.4 + 0.0085 + 11.2 + 7.8 + 1 + 13.1] \text{ mg L}^{-1}$$

$$\boxed{TDS = 120 \text{ mg L}^{-1}}$$

(e) Alkalinity is defined as:

$$ALK = \{ [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+] \} \text{ eq L}^{-1}$$

In this case:

$$[H^+] = \left( 0.32 \frac{\mu\text{g}}{\text{L}} \right) \left( \frac{1\text{g}}{10^6 \mu\text{g}} \right) \left( \frac{1 \text{ mole}}{1\text{g}} \right) = 3.2 \times 10^{-7} \text{ M}$$

$$[OH^-] = \frac{10^{-14} \text{ M}^2}{[H^+]} = \frac{10^{-14} \text{ M}^2}{3.2 \times 10^{-7} \text{ M}} = 3.13 \times 10^{-8} \text{ M}$$

$$[HCO_3^-] = \left( 58.4 \frac{\text{mg}}{\text{L}} \right) \left( \frac{1\text{g}}{10^3 \text{ mg}} \right) \left( \frac{1 \text{ mole}}{61\text{g}} \right) = 9.57 \times 10^{-4} \text{ M}$$

$$[CO_3^{2-}] = \left( 0.0085 \frac{\text{mg}}{\text{L}} \right) \left( \frac{1\text{g}}{10^3 \text{ mg}} \right) \left( \frac{1 \text{ mole}}{60\text{g}} \right) = 1.42 \times 10^{-7} \text{ M}$$

Thus:

$$ALK = [3.13 \times 10^{-8} + 9.57 \times 10^{-4} + 1.42 \times 10^{-7} - 3.2 \times 10^{-7}] \text{ eq L}^{-1}$$

$$ALK = 0.96 \text{ meq L}^{-1}$$

(f) Ionic strength is defined as:

$$I = \frac{1}{2} \sum_i C_i Z_i^2$$

where  $C_i$  is the molar concentration of species  $i$ , and  $Z_i$  is the net charge of species  $i$ . The ionic strength is calculated as follows:

| SPECIES  | MASS CONCL. $[\text{mg L}^{-1}]$ | MW $[\text{g mol}^{-1}]$ | $C_i$ $[\text{M}]$    | $Z_i$ $[-]$ | $C_i Z_i^2$ $[\text{M}]$ |
|--|----------------------------------|--------------------------|-----------------------|-------------|--------------------------|
| $\text{Ca}^{2+}$                               | 15                               | 40                       | $3.75 \times 10^{-4}$ | +2          | $1.5 \times 10^{-5}$     |
| $\text{Mg}^{2+}$                               | 4.1                              | 24                       | $1.71 \times 10^{-4}$ | +2          | $6.84 \times 10^{-5}$    |
| $\text{Na}^{+}$                                | 6.3                              | 23                       | $2.74 \times 10^{-4}$ | +1          | $2.74 \times 10^{-4}$    |
| $\text{K}^{+}$                                 | 2.3                              | 39                       | $5.90 \times 10^{-5}$ | +1          | $5.90 \times 10^{-5}$    |
| $\text{Fe}^{3+}$                               | 0.67                             | 56                       | $1.20 \times 10^{-5}$ | +3          | $2.44 \times 10^{-4}$    |
| $\text{HCO}_3^-$                               | 58.4                             | 61                       | $9.57 \times 10^{-4}$ | -1          | $9.57 \times 10^{-4}$    |
| $\text{CO}_3^{2-}$                             | 0.0085                           | 60                       | $1.42 \times 10^{-7}$ | -2          | $5.68 \times 10^{-7}$    |
| $\text{SO}_4^{2-}$                             | 11.2                             | 96                       | $1.17 \times 10^{-4}$ | -2          | $4.68 \times 10^{-4}$    |
| $\text{Cl}^{-}$                                | 7.8                              | 35.5                     | $2.20 \times 10^{-4}$ | -1          | $2.20 \times 10^{-4}$    |
| $\text{NO}_3^{-}$                              | 1                                | 62                       | $1.61 \times 10^{-5}$ | -1          | $1.61 \times 10^{-5}$    |
| $\Rightarrow I = 2.0 \times 10^{-3} \text{ M}$ |                                  |                          |                       |             |                          |

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2c)  $NCH = TH - CH = 1.1 - 0.96 \text{ meq/L} = 0.14 \text{ meq/L}$

Non carbonate hardness = 0.14 meq/L

(g) pH is defined as:

$$pH = -\log_{10}(\text{molar concentration of } H^+)$$

From part (d) we know  $[H^+] = 3.2 \times 10^{-7} \text{ M}$ .  
Therefore:

$$pH = -\log [3.2 \times 10^{-7}] = 6.5$$

(h) The following condition must be met for the electroneutrality principle to be satisfied:

$$\sum_{\text{for all anions}} C_i Z_i = \sum_{\text{for all cations}} C_i Z_i$$

We can use the values calculated in part (e) for  $C_i$  and  $Z_i$ .

For anions:

$$\begin{aligned} \sum C_i Z_i &= \{ (9.57 \times 10^{-4})(1) + (1.42 \times 10^{-7})(2) + (1.17 \times 10^{-4})(2) \\ &\quad + (2.20 \times 10^{-4})(1) + (1.61 \times 10^{-5})(1) \} \text{ M} \\ &= 1.43 \times 10^{-3} \text{ M} \end{aligned}$$

For cations:

$$\begin{aligned} \sum C_i Z_i &= \{ (3.75 \times 10^{-4})(2) + (1.71 \times 10^{-4})(2) + (2.74 \times 10^{-4})(1) \\ &\quad + (5.90 \times 10^{-5})(1) + (1.20 \times 10^{-5})(3) \} \text{ M} \\ &= 1.46 \times 10^{-3} \text{ M} \end{aligned}$$

Therefore, we have satisfied electroneutrality to within  $< 1\%$ .

### 3. Nitrogen dissolved in water

(a) The equilibrium concentration of  $N_2$  in water is determined by Henry's constant:

$$C_w = K_{H,g} P_g$$

where:

$$K_{H,g} = 0.00067 \text{ M/atm}$$

$$P_g = 0.78 \text{ atm}$$

Therefore

$$C_w = (0.00067 \frac{\text{M}}{\text{atm}})(0.78 \text{ atm})$$

$$= 5.2 \times 10^{-4} \text{ M}$$

In terms of mass concentration:

$$C_w = (5.2 \times 10^{-4} \frac{\text{moles}}{\text{L}})(28 \frac{\text{g}}{\text{mol}})$$

$$C_w = 1.46 \times 10^{-2} \frac{\text{g}}{\text{L}} = \boxed{15 \text{ mg L}^{-1}}$$

(b) Even though the Henry's constant for oxygen is twice that for nitrogen, since there is more nitrogen in air there is more nitrogen than oxygen in water exposed to the atmosphere.

### 4. Window cleaner chemistry

$$\begin{aligned} V_w &= 1 \text{ L} \\ M_T \text{ NH}_4\text{Cl} &= 10^{-3} \text{ mol} \\ \text{NH}_4\text{OH} &\rightleftharpoons \text{NH}_4^+ + \text{OH}^- \\ \text{NH}_4^+ &\rightleftharpoons \text{H}^+ + \text{NH}_3(\text{aq}) \end{aligned}$$

Unknowns:  $[\text{H}^+]$ ,  $[\text{OH}^-]$ ,  $[\text{NH}_4^+]$ ,  $[\text{NH}_3(\text{aq})]$

We can use the following equations to find the unknowns:

$$K_w = [\text{OH}^-][\text{H}^+] \rightarrow \text{equilibrium}$$

$$[\text{NH}_4^+] + [\text{NH}_3(\text{aq})] = 10^{-3} \text{ M} \rightarrow \text{mass conservation}$$

$$\frac{[\text{H}^+][\text{NH}_3(\text{aq})]}{[\text{NH}_4^+]} = K_a = 10^{-\text{p}K_a} = 10^{-9.23} \rightarrow \text{equilibrium}$$

$$[\text{H}^+] + [\text{NH}_4^+] = [\text{OH}^-] \rightarrow \text{electroneutrality}$$

We can write the terms in the electroneutrality equation as functions of  $[\text{H}^+]$  and known constants only:

$$\begin{aligned} \Rightarrow [\text{NH}_4^+] &= \frac{[\text{H}^+][\text{NH}_3(\text{aq})]}{K_a} \\ &= \frac{[\text{H}^+](10^{-3} \text{ M} - [\text{NH}_4^+])}{K_a} \\ &= \frac{10^{-3} \text{ M} [\text{H}^+]}{K_a + [\text{H}^+]} \end{aligned}$$

$$\Rightarrow [\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

Plugging back into electroneutrality:

$$[\text{H}^+] + \frac{10^{-3} \text{ M} [\text{H}^+]}{K_a + [\text{H}^+]} = \frac{K_w}{[\text{H}^+]}$$

Rearranging:

$$[\text{H}^+]^3 + (K_a + 10^{-3} \text{ M})[\text{H}^+]^2 - K_w[\text{H}^+] - K_a K_w = 0$$

Using an equation solver or computer spreadsheet to do trial and error, we get:

$$[\text{H}^+] = 8.32 \times 10^{-11} \text{ M}$$

$$\text{pH} = 10.1$$

$$\begin{aligned} K_a &= 10^{-9.23} \\ K_w &= 10^{-14} \end{aligned}$$

## 5. Elementary reaction kinetics

- (a) First-order decay of a species with concentration  $C$  can be described by the following expression:  
 $\frac{dC}{dt} = -kC$ , where  $k = 0.3 \text{ h}^{-1}$  in this case.

This expression can be integrated to solve for  $C(t)$ :  
 $\frac{dC}{dt} = -kC \Rightarrow \frac{dC}{C} = -k dt \Rightarrow \int_0^{C(t)} \frac{dC}{C} = -k \int_0^t dt$   
 $\Rightarrow \ln \frac{C}{C_0} = -kt \Rightarrow C = C_0 e^{-kt}$

We want to solve for  $t$  such that  $C = 0.10 C_0$ :  
 $0.10 = e^{-kt} \Rightarrow t = \frac{\ln(0.10)}{-0.3} = 7.7 \text{ h}$

- (b) We can use the same solution to  $C(t)$  for first-order decay we found in (a):  
 $C(t) = C_0 e^{-kt}$

We know that, at  $t = 3 \text{ h}$ ,  $C(t) = 0.20 C_0$ . Therefore:  
 $0.20 = e^{-k(3)}$   
 $\Rightarrow k = \frac{\ln(0.2)}{-3} = 0.54 \text{ h}^{-1}$

- (c) In this case, for every mole of A that reacts, one mole of B also reacts. Since there is less B than A to begin with, the reaction will proceed until B is depleted, and then the system will be at steady state. At that point:

$$\begin{aligned} B_{ss} &= 0 \text{ M} \\ A_{ss} &= A_0 - B_0 = 0.1 - 0.001 = 0.099 \text{ M} \end{aligned}$$

- (d) Considering the system from part (c) where  $A+B \rightarrow \text{products}$ , we can express the rates as:

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k[A][B]$$

From this, the characteristic time for removal of A is:  
 $\tau_A = \frac{[A]_0}{k[A]_0[B]_0} = \frac{1}{k[B]_0} = \frac{1}{(3)(0.001)} \text{ h} = 330 \text{ h}$

And the characteristic time for removal of B is:  
 $\tau_B = \frac{[B]_0}{k[A]_0[B]_0} = \frac{1}{k[A]_0} = \frac{1}{(3)(0.1)} \text{ h} = 3.3 \text{ h}$

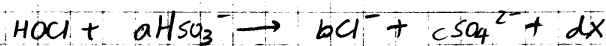
But there can't be 2 characteristic times to describe the same system. Note that all of B is consumed in the reaction, but only 1% of A. With respect to A, the reaction is not important, so  $\tau_A$  is not meaningful. Hence:

$$\tau = \tau_B = 3.3 \text{ h}$$

## 6. Redox stoichiometry

### 3.39 Redox stoichiometry

Given the following redox rxn:



- a) Oxidation state of ...

Cl in HOCl is +1

Cl<sup>-</sup> is -1

S in HSO<sub>3</sub><sup>-</sup> is +4

S in SO<sub>4</sub><sup>2-</sup> is +6

b) Doing a balance of elements on each side of equation:

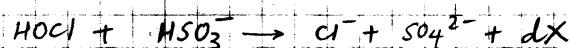
| <u>Left</u> |          | <u>Right</u> |                           |
|-------------|----------|--------------|---------------------------|
| Cl:         | 1        | b            | $\Rightarrow b = 1$       |
| S:          | a        | c            | $\Rightarrow a = c$       |
| O:          | $3a + 1$ | $4c$         | $\Rightarrow 3a + 1 = 4c$ |

$\Rightarrow 3c + 1 = 4c$   
 $c = 1$   
 $\& a = 1$

In summary,

$$\begin{aligned} a &= 1 \\ b &= 1 \\ c &= 1 \end{aligned}$$

c) We notice that Cl, S and O are balance in the Eqn. But not H.  
Substituting a, b & c in redox eqn:



$\Rightarrow$  X must be  $\text{H}^+$

Doing a balance of H in eqn:

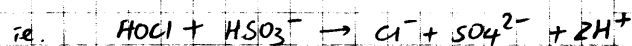
|    |             |              |
|----|-------------|--------------|
|    | <u>Left</u> | <u>Right</u> |
| H: | 2           | d            |

$\therefore d = 2$

In summary:

$$\begin{aligned} \text{X is } &\text{H}^+ \\ \& d &= 2 \end{aligned}$$

Note that the charge on both side of equation is balanced



charge on left is -1 & right is -1

Therefore we made the right guess for x!



## 7. Biochemical Oxygen Demand

$$\frac{DO(0) - DO(t)}{BOD_u} = 1 - \exp(-kt)$$

$$\exp(-kt) = 1 - \left[ \frac{DO(0) - DO(t)}{BOD_u} \right]$$

$$-kt = \ln \left[ BOD_u - DO(0) + DO(t) \right] - \ln(BOD_u)$$

$$k = \frac{1}{t} \left( \ln \left( \frac{BOD_u}{BOD_u - DO(0) + DO(t)} \right) \right) \quad (*)$$

$$BOD_u = DO(0) - DO(\infty) = \boxed{6.0 \text{ mg/L}}$$

| t (d) | DO(t) (mg/L) | k (d <sup>-1</sup> ) (*) |
|-------|--------------|--------------------------|
| 0     | 10.0         | —                        |
| 1     | 8.7          | 0.24                     |
| 2     | 7.6          | 0.26                     |
| 3     | 6.8          | 0.25                     |
| 4     | 6.2          | 0.25                     |
| 5     | 5.7          | 0.25                     |
| 6     | 5.3          | 0.25                     |
| 7     | 5.0          | 0.26                     |
| 8     | 4.8          | 0.25                     |
| 9     | 4.6          | 0.26                     |
| 10    | 4.5          | 0.25                     |
| 15    | 4.1          | 0.27                     |
| ∞     | 4.0          | —                        |

$$k = 0.25 \text{ d}^{-1}$$

$$BOD_5 = BOD_u - BOD_u e^{-kt}$$

$$= 6(1 - e^{-1.25})$$

$$BOD_5 = 4.3 \text{ mg/L}$$

## 8. Batch reactor kinetics: Sequential first-order reactions

2 sequential 1st order reactions:



a)  $\frac{d[A]}{dt} = -R_1 = -k_1 [A]$  given  $[A](0) = A_0$

$$\Rightarrow [A](t) = A_0 \exp(-k_1 t)$$

b) In order for  $[A](T) \approx A_0$ ,  $T$  must be much less than  $\tau$ , the characteristic time of rxn.

ie.  $T \ll \tau \Rightarrow T \ll \frac{1}{k_1}$

Note: When  $T \ll \frac{1}{k_1} \Rightarrow Tk_1 \ll 1$  then mathematically  
 $[A](T) = [A_0] e^{-k_1 T} \Rightarrow [A](T) = [A_0] (1 - k_1 T) \approx [A_0]$

Assuming  $[A](t) \approx A_0$  &  $k_1 \ll k_2$  for part c-f.

c)  $\frac{d[B]}{dt} = R_1 - R_2 = k_1 [A] - k_2 [B]$

$$\Rightarrow \frac{d[B]}{dt} = k_1 A_0 - k_2 [B] \quad \because [A](t) \approx A_0$$

d) At steady state,  $\frac{d[B]}{dt} = 0$

$$\Rightarrow [B]_{ss} = \frac{k_1 A_0}{k_2}$$

e) The rate of change of  $[B]$  has the form:

$$\frac{dC}{dt} = S - LC \quad \text{where } S = k_1 A_0, \quad L = k_2$$

Therefore  $\tau = \frac{1}{k_2}$  (see pages 620-621 of text)