Lafayette College
Department of Civil and Environmental Engineering

CE 321: Introduction to Environmental Engineering **Fall 2010**

Homework #9
SOLUTIONS - Due: Monday, 11/29/10 - **SOLUTIONS**

1) By volume the concentration of oxygen in air is about 21 %. Find the equilibrium concentration of O_2 in water (mole/L and mg/L) at 25°C and 1 atm of pressure. Recalculate it for Denver at an altitude of 1525m. ($P = P_o - 1.15*(10^{-4})*H$; **P** = atmospheric pressure at altitude H (atm), **H** = altitude (m), $\mathbf{P_o}$ = atmospheric pressure at sea level (atm)).

2) Suppose the gas above the soda in a bottle of soft drink is pure CO_2 at a pressure of 2 atm. Calculate $[CO_2]$ at 15°C. Also report your answer as mg/L.

3) It has been estimated that the concentration of CO_2 in the atmosphere before the Industrial Revolution was about 275 ppm (0.000275 atm = 275×10^{-6} atm). If the accumulation of CO_2 in the atmosphere continues, the by the middle of the next century it will probably be around 600 ppm (0.0006 atm = 600×10^{-6} atm). Calculate the pH of rainwater (neglecting the effect of any other gases such as H_2S and NO_2) at 25°C in each of these times.

4) If the BOD of a municipal wastewater at the end of 7 days is 60 mg/L and the ultimate BOD is 85.0 mg/L, what is the rate constant?

5) Assuming that the data in Problem 4 were taken at 25°C, computer the rate constant at 16°C.

6) A sample of municipal sewage is diluted to 1% by volume prior to running a BOD_5 analysis. After 5 days the oxygen consumption is determined to be 2.00 mg/L. What is the BOD_5 of the sewage?

7) If the BOD_5 values for two livestock wastes having *k* values of 0.3800 day^{-1} and 0.240 day^{-1} are16230.0 mg/L, what would be the ultimate BOD for each?

8) Some wastewater has a five-day BOD ate 20°C equal to 210 mg/L and an ultimate BOD of 350 mg/L. Find the five-day BOD at 25°C.

9) In a standard five-day BOD test,
   a. Why is the BOD bottle stoppered?
   b. Why is the test run in the dark (or in a black bottle)?

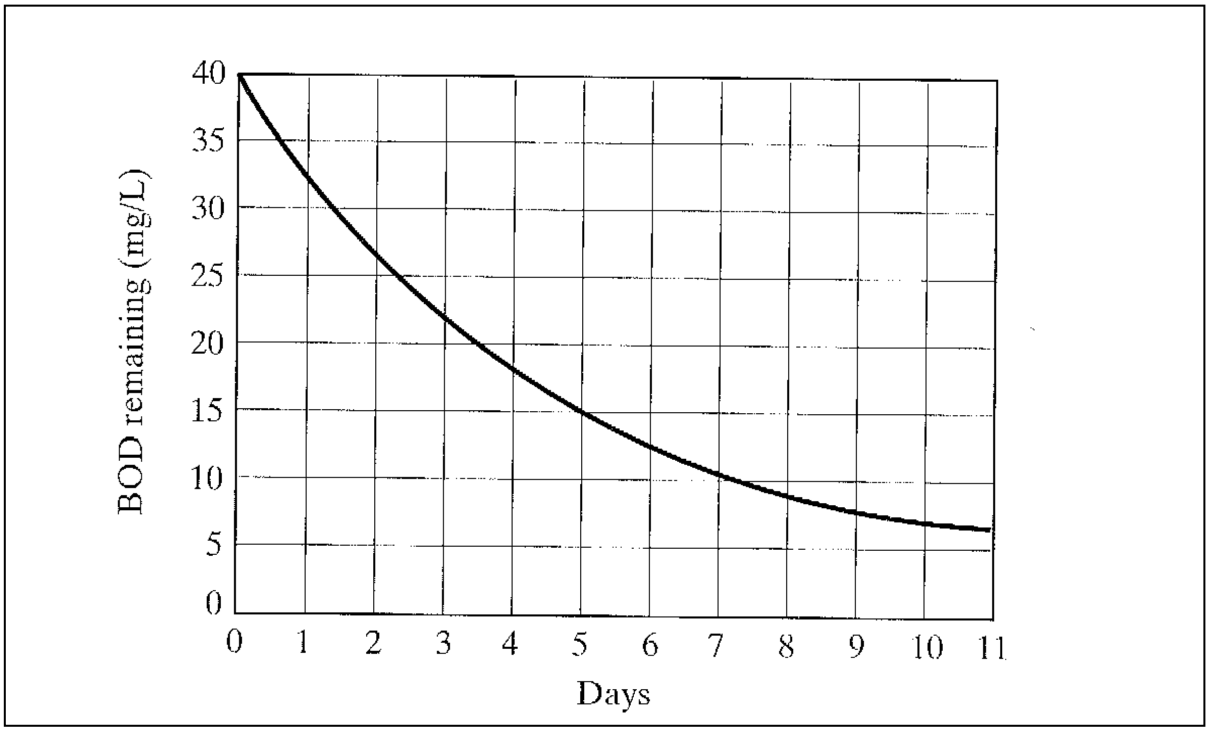
c. Why is it usually necessary to dilute the sample?
d. Why is it sometimes necessary to seed the sample?
e. Why isn't ultimate BOD measured?
f. What concentration of DO would you suggest as a starting concentration.

10) Assuming 0.1 mM of glutamic acid ($C_5H_9O_4N$) is used in the following stoichiometric reactions, calculate the NBOD of glutamic acid.

$$C_5H_9O_4N + 4.5O_2 \rightarrow 5CO_2 + 3H_2O + NH_3$$
$$NH_3 + 2O_2 \rightarrow NO_3^- + H^+ + H_2O$$

11) If the dissolved oxygen concentration measured during a BOD test is 9 mg/L initially, 6 mg/L after 5 days, and 3 mg/L after an indefinitely long period of time, calculate the 10-day BOD.

12) The following figure shows a plot of BOD remaining versus time for a sample of the effluent taken from a wastewater treatment plant.
a. What is the ultimate BOD (L_o)?
b. What is the five-day BOD?
c. What is L_t for 7 days?



13) If the BOD_5 for some wastewater if 200 mg/L and the ultimate BOD is 300 mg/L, find the reaction rate constant k (base e) and K (base 10).

14) Suppose some wastewater had a BOD_5 equal to a 180 mg/L and a reaction rate k equal to 0.22/day. It also has total Kjedahl nitrogen content (TKN) of 30 mg/L.
    a. Find the ultimate carbonaceous oxygen demand (CBOD).
    b. Find the ultimate nitrogenous oxygen demand (NBOD).
    c. Find the remaining BOD (nitrogenous plus carbonaceous) after five days have elapsed.

15) Glutamic acid ($C_5H_9O_4N$) is used as one of the regent for a standard to check the BOD test. Determine the theoretical oxygen demand of 150 mg/L of glutamic acid. Assuming the following reactions:

$$C_5H_9O_4N + 4.5O_2 \rightarrow 5CO_2 + 3H_2O + NH_3$$
$$NH_3 + 2O_2 \rightarrow NO_3^- + H^+ + H_2O$$

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#1 By volume the concentration of oxygen in air is about 21%. Find the equilibrium concentration of O_2 in water (mole/L and mg/L) at 25°C and 1 atm of pressure. Recalculate it for Denver at an altitude of 1525 m.
$P = P_o - 1.15\times(10^{-4})H$; P = atmospheric pressure at altitude H
H = altitude (m), P_o = atmospheric pressure at sea level (atm)

$P_{O_2} = 21\% \cdot (1\,atm) = 0.21\,atm$

$K_H\ @\ 25°C = 0.001233\ M/atm$

$[O_2] = K_H \cdot P_{O_2} = 0.001233\ M/atm \cdot 0.21\,atm$

$\boxed{[O_2] = 2.5893\times10^{-4}\ M}$

$= 2.5893\times10^{-4}\ mol/L \cdot 32\ g/mol = \boxed{8.286\ mg/L}$

$P = 1\,atm - 1.15\times10^{-4}\times1525\,m = 0.825\,atm$

$P_{O_2} = 21\% \cdot 0.825\,atm = 0.173\,atm$

$[O_2]_H = 0.001233\ M/atm \cdot 0.173\,atm$

$\boxed{[O_2]_H = 2.135\times10^{-4}\ M} =$

$= 2.135\times10^{-4}\ mol/L \times 32\ g/mol = \boxed{6.833\ mg/L}$

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#2 Suppose the gas above the soda in a bottle of soft drink is pure CO_2 at a pressure of 2 atm. Calculate $[CO_2]$ at 15°C. Also, report your answer as mg/L.

$$[CO_2] = K_H \cdot P_g \quad \text{(Henry's Law)}$$

$$K_H = 0.045726\ M/atm$$

$$P_g = 2\ atm.$$

$$\Rightarrow \boxed{[CO_2] = 0.09145\ M}$$

$$[CO_2] = 0.09145\ mol/L \cdot 44000\ mg/mol = \boxed{4023.8\ mg/L}$$

$$M_{CO_2} = 12 + 2 \times 16 = 44\ g/mol$$

#3 It has been estimated that the concentration of CO_2 in the atmosphere before the Industrial Revolution was about 275 ppm. If the accumulation of CO_2 in the atmosphere continues, then by the middle of the next century it will probably be around 600 ppm. Calculate the pH of rainwater (neglecting the effect of any other gasses such as H_2S and NO_2) at 25°C in each of these times.

$$[H^+] = [HCO_3^-] + 2\cancel{[CO_3^{-2}]} + [OH^-]$$

we can eliminate this based on our understanding of CO_3^{-2} in water & pH

$$[H^+][OH^-] = K_w = 10^{-14}$$

$$[H^+] \approx [HCO_3^-] + [OH^-] = [HCO_3^-] + \frac{10^{-14}}{[H^+]}$$

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+ \qquad k_1$$

$$k_1 = \frac{[HCO_3^-][H^+]}{[CO_2]} \Rightarrow [HCO_3^-] = \frac{k_1[CO_2]}{[H^+]}$$

$$[H^+] = \frac{k_1[CO_2] + 10^{-14}}{[H^+]}$$

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$$[H^+]^2 = k_1 [CO_2] + 10^{-14}$$

$$[CO_2] = k_H \cdot P_g \qquad k_H @ 25°C = 0.033363 \ mol/L\cdot atm$$

275 ppm $\rightarrow$ 0.000275 atm = 275×10^{-6} atm.
600 ppm $\rightarrow$ 0.0006 atm = 600×10^{-6} atm.

$$[CO_2]_1 = 0.033363 \ mol/L\,atm \cdot (275 \times 10^{-6} \ atm)$$
$$= 9.175 \times 10^{-6} \ mol/L$$

$$[CO_2]_2 = 0.033363 \ mol/L\cdot atm \cdot (600 \times 10^{-6} \ atm)$$
$$= 20.018 \times 10^{-6} \ mol/L$$

$$[H^+]_1^2 = (4.47 \times 10^{-7} \times 9.175 \times 10^{-6} + 10^{-14}) \ mol/L \Rightarrow$$
$$\Rightarrow [H^+]_1 = 2.028 \times 10^{-6} \ mol/L \Rightarrow pH_1 = -\log [H^+]_1 \Rightarrow$$
$$\Rightarrow \boxed{pH_1 = 5.69} \ @ \ 275 \ ppm$$

$$[H^+]_2^2 = (4.47 \times 10^{-7} \times 20.018 \times 10^{-6} + 10^{-14}) \ mol/L \Rightarrow$$
$$\Rightarrow [H^+]_2 = 2.993 \times 10^{-6} \ mol/L \Rightarrow pH_2 = -\log [H^+]_2$$
$$\Rightarrow \boxed{pH_2 = 5.52} \ @ \ 600 \ ppm$$

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#4 $\boxed{8-4}$ If the BOD of a municipal wastewater at the end of 7 days is 60.0 mg/L and the ultimate BOD is 85.0 mg/L, what is the rate constant?

$BOD_7 = 60.0$ mg/L
$L_o = 85.0$ mg/L
$t = 7$ days

$k = ?$

$$BOD_7 = L_o\left(1 - e^{-k \cdot 7}\right)$$

$$\frac{BOD_7}{L_o} = 1 - e^{-7k}$$

$$-\left(\frac{BOD_7}{L_o} - 1\right) = e^{-7k} \Rightarrow$$

$$\Rightarrow \ln\left(\frac{-BOD_7 + L_o}{L_o}\right) = -7k \ln e \Rightarrow k = \frac{\ln\left(\frac{-BOD_7 + L_o}{L_o}\right)}{-7}$$

$$\Rightarrow k = \frac{\ln\left[\frac{(-60.0 + 85.0)\ mg/L}{85.0\ mg/L}\right]}{-7} = 0.1748$$

$$\boxed{k = 0.1748/day}$$

#5 $\boxed{8-8}$ Assuming that the data in problem 8-4 were taken at 25°C, compute the rate constant at 16°C

$$K_{25} = K_{20} \cdot \theta^{(25-20)} \qquad \left.\begin{array}{l}\theta = 1.056 \\ K_{25} = 0.1748\end{array}\right\} \Rightarrow$$

$$\Rightarrow K_{20} = \frac{0.2067}{1.056^5} = 0.1331$$

$$K_{16} = K_{20} \cdot \theta^{(16-20)} \qquad \theta = 1.135$$

$$K_{16} = (0.1331) \cdot 1.135^{-4} \Rightarrow \boxed{K_{16} = 0.0802/day}$$

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#6 $\boxed{8-9}$ A sample of municipal sewage is diluted to 1% by volume prior to running a BOD_5 analysis. After 5 days the oxygen consumption is determined to be 2.00 mg/L. What is the BOD_5 of the sewage?

$$BOD_{5\,dil} = 2.00\ mg/L$$

$$BOD_{5\,sewage} \cdot 1\% = BOD_{5\,dil}$$

$$BOD_{5\,sewage} = \frac{BOD_{5\,dil}}{0.01} = \frac{2.00\ mg/L}{0.01}$$

$$\boxed{BOD_{5\,sewage} = 200\ mg/L}$$

$\boxed{\#7}$ $\boxed{8-12}$ If the BOD_5 values for two livestock wastes having k values of 0.3800/day and 0.240/day are both 16230.0 mg/L, what would be the ultimate BOD for each?

$$BOD_5 = L_o(1-e^{-k5}) \Rightarrow L_o = \frac{BOD_5}{1-e^{-5k}}$$

$$L_o = \frac{16230.0\ mg/L}{1-e^{-5days \times 0.3800/day}} = \boxed{19{,}084.4\ mg/L}$$

$$L_o = \frac{16230.0\ mg/L}{1-e^{-5days \times 0.240/day}} = \boxed{23{,}225.3\ mg/L}$$

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#8 Some wastewater has a five-day BOD at 20°C equal to 210 mg/L and an ultimate BOD of 350 mg/L. Find the five-day BOD at 25°C.

ultimate BOD : $L_0 = 350$ mg/L
$BOD_5 = 210$ mg/L

$$BOD_5 = L_0 \left(1 - e^{-k \cdot 5}\right) \Rightarrow \frac{BOD_5}{L_0} - 1 = -e^{-k5}$$

$$1 - \frac{BOD_5}{L_0} = e^{-k5} \Rightarrow \ln\left(1 - \frac{BOD_5}{L_0}\right) = -k5$$

$$\Rightarrow k = \frac{\ln\left(1 - \frac{BOD_5}{L_0}\right)}{-5} = \frac{\ln\left(1 - \frac{210 \text{ mg/L}}{350 \text{ mg/L}}\right)}{-5}$$

$$k_{20} = 0.183$$

$$k_{25} = k_{20} \cdot \theta^{(25-20)} = 0.183 \cdot (1.056)^5 = 0.241$$

$$BOD_5 (\text{at } 25°C) = L_0 \left(1 - e^{-k_{25} \cdot t}\right)$$
$$= 350 \text{ mg/L} \cdot \left(1 - e^{-0.241 \cdot 5}\right)$$

$$\boxed{BOD_5 (\text{at } 25°C) = 244.92 \text{ mg/L}}$$

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$\boxed{\#9}$ In a standard five-day BOD test,

a. Why is the BOD bottle stoppered?

The BOD bottle is stoppered to exclude air bubbles.

b. Why is the test run in the dark (or in a black bottle)?

The test is run in the dark to prevent photosynthesis from adding oxygen to the water and invalidating the oxygen consumption results.

c. Why is it usually necessary to dilute the sample?

The samples are usually diluted because the only oxygen available to the organisms is dissolved in water. The most oxygen that can dissolve is about 9 mg/L, so the BOD of the diluted sample should be in the range of 2 to 6 mg/L.

d. Why is it sometimes necessary to seed the sample?

It is sometimes necessary to seed the sample, meaning to put live bacteria into water so that the degradation of the organic matter is not limited by the lack of bacterial growth. The microorganisms are basically introduced in the water to ensure the supply of oxygen meets the demand.

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e. Why isn't ultimate BOD measured?

We don't measure the ultimate BOD because it has become tradition to measure the BOD after 5 days. The 5 day BOD was chosen by sanitary engineers in England, where the River Thames has a travel time to the sea of less than 5 days. Because no other time is any more rational than 5 days, this value has become tradition & UBOD would take too long

f. What concentration of DO would you suggest as a starting point?

The concentration of DO at the starting point should be as high as possible. Since the most oxygen that can dissolve in water is about 9 mg/L, that is the concentration of DO I would suggest as a starting point.

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#10 $\boxed{8-13}$ Using the data from 8-1, calculate the NBOD of glutamic acid. Assume the concentration of glutamic acid is 0.1 mM.

$$C_5H_9O_4N + 4.5O_2 \rightarrow 5CO_2 + 3H_2O + NH_3.$$

$$0.1\,mM\ C_5H_9O_4N \times \frac{4.5\ mol\ O_2}{1\ mol\ C_5H_9O_4N} = 0.45\,mM\ O_2$$

$$\boxed{CBOD} = 0.45\,mM\ O_2 \times 32\ mg/mmol = \boxed{14.4\ mg/L}$$

$$NH_3 + 2O_2 \rightarrow NO_3^- + H^+ + H_2O$$

$$0.1\,mM\ C_5H_9O_4N \times \frac{1\ mol\ NH_3}{1\ mol\ C_5H_9O_4N} = 0.1\,mM\ NH_3$$

$$0.1\,mM\ NH_3 \times \frac{2\ mol\ O_2}{1\ mol\ NH_3} = 0.2\,mM\ O_2$$

$$\boxed{NBOD} = 0.2\,mM\ O_2 \times 32\ mg/mmol = \boxed{6.4\ mg/L}$$

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#11 If the dissolved oxygen concentration measured during a BOD test is 9 mg/L initially, 6 mg/L after 5 days, and 3 mg/L after an indefinitely long period of time, calculate the 10 day BOD.

$$BOD_5 = DO_{init} - DO_5 = 9\,mg/L - 6\,mg/L = 3\,mg/L$$

$$L_0 = DO_{init} - DO_u = 9\,mg/L - 3\,mg/L = 6\,mg/L$$

$$\Rightarrow \quad BOD_5 = L_0\left(1 - e^{-k\cdot 5}\right)$$

$$\frac{3\,mg/L}{6\,mg/L} = 1 - e^{-k\cdot 5}$$

$$\frac{1}{2} - 1 = -e^{-k\cdot 5} \Rightarrow \ln\left(\frac{1}{2}\right) = -k\cdot 5 \ln e \Rightarrow$$

$$\Rightarrow k = \frac{-\ln(2)}{-5} \Rightarrow \boxed{k = 0.1386\ /day}$$

$$BOD_{10} = L_0\cdot\left(1 - e^{-k\cdot 10}\right) = 6\,mg/L\left(1 - e^{-0.1386\cdot 10}\right)$$

$$\boxed{BOD_{10} = 4.50\ mg/L}$$

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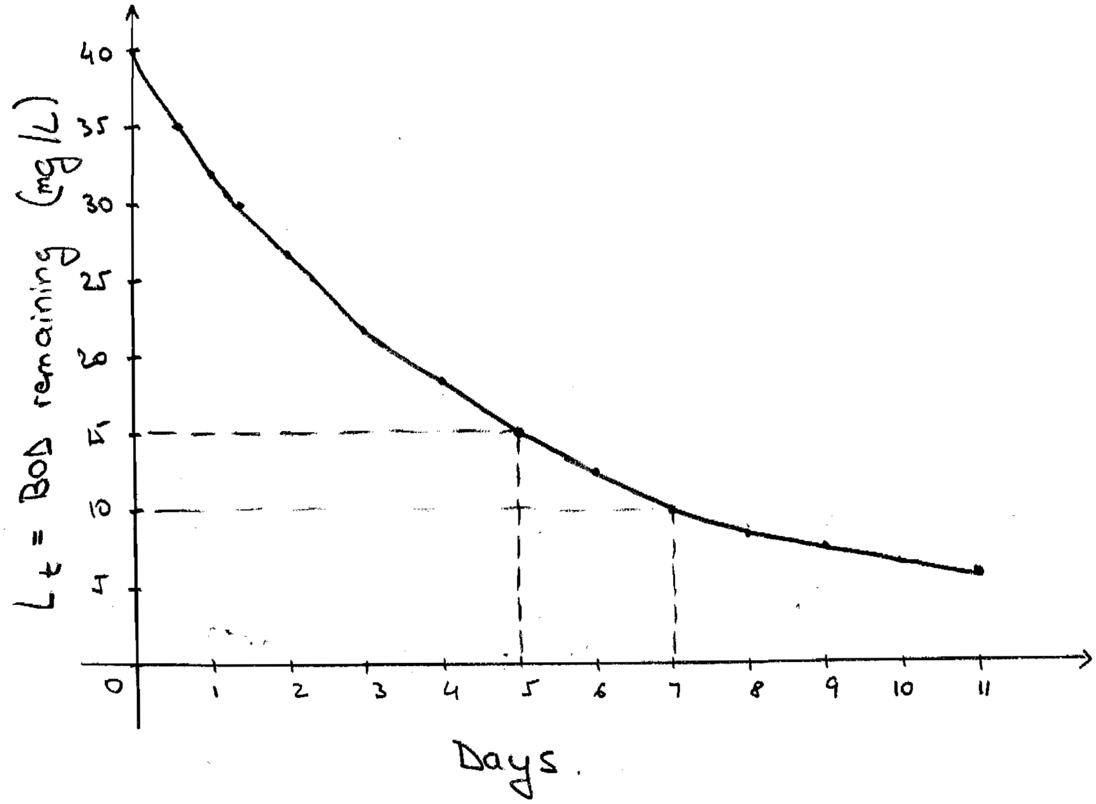
|#12| The following figure shows a plot of BOD remaining versus time for a sample of effluent taken from a wastewater treatment plant.



a) What is the ultimate BOD (L_o)?

Ultimate BOD = $\boxed{L_o = 40\ mg/L}$

b) What is the five-day BOD?

$L_o = L_t + BOD_t \Rightarrow BOD_5 = L_o - L_t$

$BOD_5 = 40\ mg/L - 15\ mg/L \Rightarrow \boxed{BOD_5 = 25\ mg/L}$

c) What is L_t for 7 days?

$\boxed{L_t = 10\ mg/L}$

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$\boxed{\#13}$ If the BOD_5 for some wastewater is 200 mg/L and the ultimate BOD is 300 mg/L find the reaction rate constant k (base e) and K (base 10).

$BOD_5 = 200\ mg/L$	
$L_0 = 300\ mg/L$	
$k = ?$	$K = ?$

$$BOD_t = L_0(1 - e^{-kt})$$

$$BOD_t = L_0(1 - 10^{-Kt})$$

$$200\ mg/L = 300\ mg/L\ (1 + e^{-k \cdot 5}) \Rightarrow \frac{2}{3} - 1 = -e^{-5k}.$$

$$\Rightarrow \ln\left(\frac{1}{3}\right) = -5k \ln e \Rightarrow k = -\frac{\ln(3)}{-5} = 0.2197$$

$$\Rightarrow \boxed{k = 0.2197/day}$$

$$200\ mg/L = 300\ mg/L\ (1 - 10^{-K \cdot 5})$$

$$\frac{2}{3} - 1 = -10^{-5K} \Rightarrow \log\left(\frac{1}{3}\right) = -5K \log 10$$

$$\Rightarrow K = \frac{-\log(3)}{-5} = 0.0954 \Rightarrow \boxed{K = 0.0954/day}$$

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#14 Suppose some wastewater had a BOD_5 equal to a 180 mg/L and a reaction rate k equal to 0.22/day. It also has a total Kjedahl nitrogen content of (TKN) 30 mg/L.

a. Find the ultimate carbonaceous oxygen demand (CBOD)

$$BOD_t = L_o(1 - e^{-kt})$$

$$L_o = \text{BOD Ultimate} = BOD_u \Rightarrow L_o = BOD_5 / (1 - e^{-k \cdot 5})$$

$$BOD_5 = 180 \text{ mg/L} \qquad k = 0.22/\text{day}$$

$$L_o = 180 \text{mg/L} / [1 - e^{(-0.22/\text{day} \cdot 5\text{days})}] = \boxed{269.81 \text{ mg/L}}$$

b. Find the ultimate nitrogenous oxygen demand (NBOD)

$$NBOD = (4.57 \text{ mg } O_2/\text{mg N}) \cdot (\underset{\uparrow \text{TKN}}{X} \text{ mg N})$$

$$NBOD = 4.57 \text{ mg } O_2/\text{mg N} \cdot 30 \text{ mg N/L} = \boxed{137.1 \text{ mg } O_2/L}$$

c. Find the remaining BOD (nitrogenous plus carbonaceous) after five days have elapsed.

$$\text{Remaining BOD at 5 days} = \text{Total BOD} - BOD_5 =$$

$$= 269.81 \text{ mg/L} + 137.1 \text{ mg/L} - 180 \text{ mg/L} = \boxed{226.9 \text{ mg/L}}$$

or, $= L_t + NBOD$

$$L_t = L_o \cdot e^{-kt} = 269.81 \text{ mg/L} \cdot e^{-0.22 \cdot 5} = 89.81 \text{ mg/L}$$

$$\text{Remaining BOD at 5 days} = 89.81 \text{ mg/L} + 137.1 \text{ mg/L} =$$

$$= \boxed{226.91 \text{ mg/L}}$$

15) Glutamic acid ($C_5H_9O_4N$) is used as one of the regent for a standard to check the BOD test. Determine the theoretical oxygen demand of 150 mg/L of glutamic acid. Assuming the following reactions:

$$C_5H_9O_4N + 4.5O_2 \rightarrow 5CO_2 + 3H_2O + NH_3$$
$$NH_3 + 2O_2 \rightarrow NO_3^- + H^+ + H_2O$$

Given: 150 mg · L^{-1} of glutamic acid and oxidation reactions
Solution:

a. Compute the gram molecular weights of glutamic acid and oxygen consumed
MW of $C_5H_9O_4N$ = 147
MW of oxygen (4.5 O_2 + 2 O_2) = 208
b. Calculate the ThOD

TOD -(150mg/L) (208/147)= 212mg/L