Problems And Solutions
On
DO, BOD, COD, ThOD, TOC

Solubility of Oxygen

- What is the solubility of oxygen in water in contact with air when the atmospheric pressure is 0.88 atm, the temperature is 16°C, and the chloride concentration is 1000 mg/L?

Henry Constants for Various Gases

Table 1: Some forms of Henry's law and constants (gases in water at 298 K), derived from [4]				
equation:	$k_{H,pc} = \frac{p}{c}$	$k_{H,cp} = \frac{c}{p}$	$k_{H,px} = \frac{p}{x}$	$k_{H,cc} = \frac{c_{aq}}{c_{gas}}$
units:	$\frac{L \cdot atm}{mol}$	$\frac{mol}{L \cdot atm}$	atm	*dimensionless*
O_2	769.23	1.3×10^{-3}	4.259×10^{4}	3.180×10^{-2}
H_2	1282.05	7.8×10^{-4}	7.099×10^{4}	1.907×10^{-2}
CO_2	29.41	3.4×10^{-2}	0.163×10^{4}	0.8317
N_2	1639.34	6.1×10^{-4}	9.077×10^{4}	1.492×10^{-2}
He	2702.7	3.7×10^{-4}	14.97×10^{4}	9.051×10^{-3}
Ne	2222.22	4.5×10^{-4}	12.30×10^{4}	1.101×10^{-2}
Ar	714.28	1.4×10^{-3}	3.955×10^{4}	3.425×10^{-2}
CO	1052.63	9.5×10^{-4}	5.828×10^{4}	2.324×10^{-2}

c = amount concentration of gas in solution (in mol/L)
p = partial pressure of gas above the solution (in atm)
x = mole fraction of gas in solution (dimensionless

$$P = 0{,}88\ atm \Rightarrow P_{O_2} = (0{,}21) \times (0{,}88\ atm) = 0{,}185\ atm$$

$$O_2(g) \underset{}{\overset{K_H}{\rightleftharpoons}} O_2(aq)$$

$$O_2(aq) = K_H \times O_2(g)\ ;\ K_{H,O_2} = 1{,}3 \times 10^{-3} \frac{mol}{L \cdot atm}$$

$$O_2(aq) = \left(1{,}3 \times 10^{-3} \frac{mol}{L \cdot atm}\right) \times (0{,}185\ atm) = 2{,}4 \times 10^{-4} \frac{mol}{L}$$

$$O_2(aq) = 2{,}4 \times 10^{-4} \frac{mol}{L} \times \frac{32\,gr}{1\,mol} \times \frac{1000\,mg}{1\,gr}$$

$$O_2(aq) = 7{,}69\ mg/L \text{ (25°C and no salinity)}$$

Temperature dependence of Henry constant

- Liq→Gas : $k_{\mathrm{H,pc}}(T) = k_{\mathrm{H,pc}}(T^{\ominus}) \exp\left[-C\left(\frac{1}{T}-\frac{1}{T^{\ominus}}\right)\right]$
- Gas→Liq : $k_{\mathrm{H,cp}}(T) = k_{\mathrm{H,cp}}(T^{\ominus}) \exp\left[C\left(\frac{1}{T}-\frac{1}{T^{\ominus}}\right)\right]$
- $\boldsymbol{k}_{\mathrm{H}}$: Henry's constant for a given temperature,
- $\boldsymbol{T}$: any given temperature, in K,
- $\boldsymbol{T}^{\ominus}$: standard temperature (298 K)
- **Values of *C* (in K).**

Gas	O_2	H_2	CO_2	N_2	He	Ne	Ar	CO
C	1700	500	2400	1300	230	490	1300	1300

Solubility of O_2 against Temp and Salinity

Temperature, °C	Chloride concentration, mg/L 0	5000	10,000	15,000	20,000
0	14.6	13.8	13.0	12.1	11.3
1	14.2	13.4	12.6	11.8	11.0
2	13.8	13.1	12.3	11.5	10.8
3	13.5	12.7	12.0	11.2	10.5
4	13.1	12.4	11.7	11.0	10.3
5	12.8	12.1	11.4	10.7	10.0
6	12.5	11.8	11.1	10.5	9.8
7	12.2	11.5	10.9	10.2	9.6
8	11.9	11.2	10.6	10.0	9.4
9	11.6	11.0	10.4	9.8	9.2
10	11.3	10.7	10.1	9.6	9.0
11	11.1	10.5	9.9	9.4	8.8
12	10.8	10.3	9.7	9.2	8.6
13	10.6	10.1	9.5	9.0	8.5
14	10.4	9.9	9.3	8.8	8.3
15	10.2	9.7	9.1	8.6	8.1
16	10.0	9.5	9.0	8.5	8.0
17	9.7	9.3	8.8	8.3	7.8
18	9.5	9.1	8.6	8.2	7.7
19	9.4	8.9	8.5	8.0	7.6
20	9.2	8.7	8.3	7.9	7.4
21	9.0	8.6	8.1	7.7	7.3
22	8.8	8.4	8.0	7.6	7.1
23	8.7	8.3	7.9	7.4	7.0
24	8.5	8.1	7.7	7.3	6.9
25	8.4	8.0	7.6	7.2	6.7
26	8.2	7.8	7.4	7.0	6.6
27	8.1	7.7	7.3	6.9	6.5
28	7.9	7.5	7.1	6.8	6.4
29	7.8	7.4	7.0	6.6	6.3
30	7.6	7.3	6.9	6.5	6.1

- From the Table:
  at 25C → DO : 8.4 mg/L
  at 16C → DO : 10.0 mg/L
- This Table **does involve** the temp dependence of K_H

- Use a simple direct proportion rule and find DO at 16C for 0.88 atm, i.e.: At 16 C:
  For 1 atm → DO : 10.0 mg/L
  For 0.88 atm → DO: ?
- Then, use again simple proportion to find DO for 1000mg/L salinity (intrapolation between 0 -5000 mg/L salinity). i.e.,
  For 0 mg/L salinity → DO : 10.0 mg/L
  For 5000 mg/L salinity → DO : 9.5 mg/L

Solubility of Oxygen

- Calculate the percent saturation of dissolved oxygen in a water sample with a temperature of 22°C and a dissolved-oxygen concentration of 5.3 mg/L when the atmospheric pressure is 1 atm. Assume the sample salinity is less than 100 *mgIL.*

- From the Table

  At 22 C → DO : 8.8 m/L which is the saturation concn.
- Then,
- **% Saturation =** (8.8 – 5.3) / 8.8 = **66 %**

- The effect of salinity may be assumed to be negligeble since it is close to zero…

Theoretical COD

- What is the theoretical COD of samples containing 300 mg/L of
- (a) ethanol (C_2H_5OH),
- (b) phenol (C_6H_5OH), and
- (c) leucine ($C_6H_{13}NO_2$)?

Theoretical COD

- As an example, lets work on phenol,
- The theoretical oxidation rxn is as follow:

  C_6H_5OH + 7 O_2 → 6 CO_2 + 3 H_2O

  94 gr 224 gr

  300 mg/L **715 mg/L : Theoretical COD**
- **---**
- $C_6H_{13}NO_2$ + …. O_2 → 6 CO_2 + …. H_2O + NO_3

  Complete the stoichiometry and do the rest of the calculations….

Theoretical COD and estimation of L_0

- ***(a)*** *Estimate the COD of a solution containing 500 mgIL of butanol (C_4H_9OH)*
- ***(b)*** *If the compound were readily degradable biologically, about what would you* expect the 5-day BOD to be?

- **Solution:**
- **(a)** You know how to calculate ThCOD…

  C_4H_9OH + …O_2 → 4 CO_2 + …H_2O

- **(b)** Use the Table 23.2 in the text to estimate the percentage of BOD_5 as follows

Theoretical COD and estimation of L_0

- Choose a k value for the highest biodegradability and estimate 5-day BOD…

Table 23.2 | Significance of reaction rate constant k' upon BOD

Time, days	Percent of total BOD exerted				
	k' = 0.10	0.20	0.30	0.40	0.50
1	10	18	26	33	39
2	18	33	45	55	63
3	26	45	59	70	78
4	33	55	70	80	86
5	39	63	78	86	92
6	45	70	83	91	95
7	50	75	88	94	97
10	63	86	95	98	99
15	78	95	99	99+	99+
20	86	98	99+	99+	99+

Notations about BOD

- Ultimate BOD : L_0 or BOD_u
- BOD at any time : y_t or BOD_t
- 5-day BOD : y_5 or BOD_5
- k_{20} : rate constant at temp 20 C
- k_T : rate constant at temp T

BOD and Biodergadability

- What could be inferred from the following analytical results concerning the relative ease of biodegradability of each waste?

Waste	5-day BOD, mg/L	COD, mg/L
A	240	300
B	100	500
C	120	240

5-day BOD test

$$\text{BOD (mg/l)} = \frac{D_0 - D_5}{P}$$

P is decimal volumetric fraction of wastewater used in test

D is dissolved oxygen concentration at Time=0 and Time = 5 days

BOD and Pollution Flowrate

- A wastewater stream has a BOD of 4000 mg/L. Calculate the flowrate of BOD (in kg/hr) if the wastewater has a flowrate of 5000 m^3/hr. Assume, if necessary, the density of wastewater as 1,05 gr/cm^3
- **Solution:**
- BOD Flowrate in kg/hr =
- (5000 m^3/hr) x (4000 mg/L) x
- (1 kg/10^6mg) x(10^3 L/1 m^3) = 200 kg/hr

Time dependent BOD values

- A sample of wastewater has an ultimate BOD of 280mg/L and a 5-day BOD of 240mg/L. Calculate 20-day BOD of this sample.
- **Solution:**

  $y_{20} = L_0 (1-e^{-k*20})$:

  <u>First calculate ***k*** using given data</u>

  $y_5 = L_0 (1-e^{-k*5}) \rightarrow 240 = 280 (1-e^{-k*5}) \rightarrow$ **k = 0.39 d^{-1}**

 Then 20-day BOD:

  $y_{20} = L_0 (1-e^{-k*20}) = 280 (1-e^{-0.39*20}) = 279.9$ mg/L

Time dependent BOD values

- $y_1 = L_0 \, (1-e^{-k*t1})$
- $y_2 = L_0 \, (1-e^{-k*t2})$

- $y_1/y_2 = (1-e^{-k*t1}) \, / \, (1-e^{-k*t2})$

- If 2 different days of BODs are known, ***k*** value can be calculated. Then L_0 can be calculated….

Sample Calculation for BOD

Determine the 5-day BOD for a 15 ml sample that is diluted with dilution water to a total volume of 300 ml when the initial DO concentration is 8 mg/l and after 5 days, has been reduced to 2 mg/l.

$D_0 = 8$
$D_5 = 2$
$P = 15 \text{ ml}/300\text{ml} = 0.05$

$$\text{BOD (mg/l)} = \frac{8 - 2}{0.05} = 120$$

Sample Calculation for BOD

Example: Calculation of BOD values

- The BOD of a wastewater is suspected to range from 50 to 200 mg/l. Three dilutions are prepared to cover this range. The procedure is the same in each case. First the sample is placed in the standard BOD bottle and is then diluted to 300 ml with organic-free, oxygen-saturated water. The initial DO is determined and the bottles tightly stoppered and placed in the incubator at 20°C for 5 days, after which the DO is again determined. If the third value is disregarded (the final DO being less than 2 mg/l), calculate the average BOD.

Sample Calculation for BOD

Wastewater, ml	DO_I, mg/l	DO_F, mg/l	O_2 used, mg/l	P	BOD_5, mg/l
5	9.2	6.9	2.3	0.0167	138
10	9.1	4.4	4.7	0.033	142
20	8.9	1.5	7.4	0.067	110

If the third value is disregarded (final DO is less than 2 mg/l) then the average BOD value is (138 + 142)/2 = 140 mg/l

Sample Calculation for BOD

Question: The BOD5 of a wastewater is determined to be 150 mg/l at 20oC. The k value is known to be 0.23 per day. What would be the BOD8 be if the test were run at 15oC?

a) Determine the ultimate BOD:

$$y_u = \frac{y_5}{1 - e_{-kt}}$$

$$y_u = \frac{150}{1 - e^{-0.23x5}} = 220 mg/l$$

Sample Calculation for BOD

- b) Correct the k value for 15 C
- $k_T = k_{20}\ \Theta^{T-20}$

  $k_{15} = 0.23\ (1.047^{15-20}) = 0.18\ d^{-1}$

- c) Calculate y_8

  $y_8 = 220\ (1 - e^{0.18x8}) = 168$ mg/L

Sample Calculation for BOD

BOD_u and BOD_5

$$BOD_t = BOD_u(1 - e^{-k_1 t})$$

- So, if the BOD_5 of a waste discharge is 250 mg L^{-1}, and k_1 is 0.46 d^{-1}:

  $250 = BOD_u\,(1\text{-}e^{-0.46x5})$

  $BOD_u = 250/(1 - e^{-0.46x5}) = 277.8$ mg L^{-1}

Thomas Method

- Various ways exist to determine ***k*** and ***BODu***. The method we will use is the Thomas method *Water Sewage and Works, Vol. 97 pg. 123, 1950.*
- *Thomas recognized the similarity of the series expansions* for $1\text{-}e^{-kt}$ and $kt[1+(kt/6)]^{-3}$ and the BOD equation and developed the approximate formula:

$$BOD = k \cdot BOD_u \cdot t\left(1 + \frac{k \cdot t}{6}\right)^{-3}$$

Thomas Method

$$1 - e^{-kt} = kt\left[1 - \frac{kt}{2!} + \frac{(kt)^2}{3!} - \frac{(kt)^3}{4!} + \dots\right]$$

$$kt\left(1 + \frac{kt}{6}\right)^{-3} = kt\left[1 - \frac{kt}{2} + \frac{(kt)^2}{6} - \frac{(kt)^3}{21.6} + \dots\right]$$

$$(1 - e^{-kt}) \cong kt\left(1 + \frac{kt}{6}\right)^{-3}$$

$$\Rightarrow \quad y = L_0\,(1 - e^{-kt})$$

$$y = L_0\,kt\left(1 + \frac{kt}{6}\right)^{-3}$$

Thomas Method

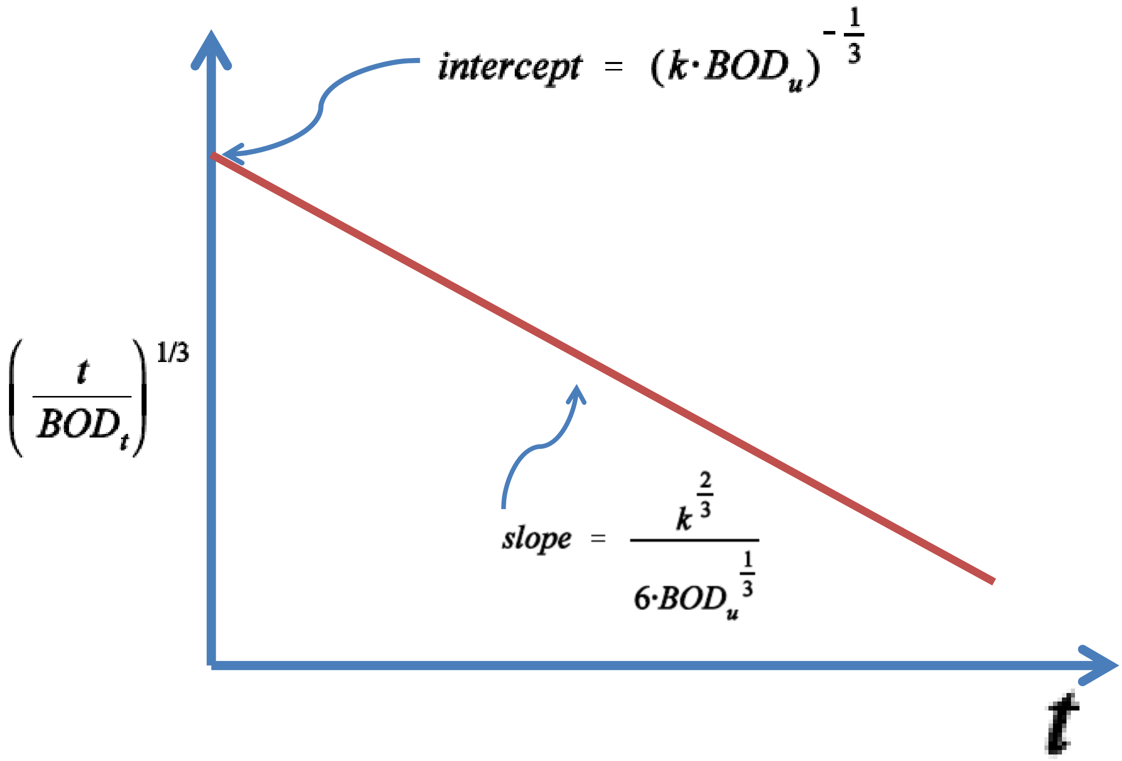
- linearizing gives (how to linearize?)

$$\left(\frac{t}{BOD_t}\right)^{1/3} = (kBOD_u)^{-1/3} + \frac{k^{2/3}}{6 \cdot BOD_u^{1/3}}\, t$$

- Plotting **(t/BOD)$^{1/3}$** vs **t** gives a straight line, where

$$slope = \frac{k^{\frac{2}{3}}}{6 \cdot BOD_u^{\frac{1}{3}}} \qquad intercept = (k \cdot BOD_u)^{-\frac{1}{3}}$$

Thomas Method



Example on Thomas Method

Time (1) d	Measured BOD (3) mg/L
0.5	5
1.0	20
2.0	90
3.0	160
4.0	200
5.0	220
7.0	260
10.0	285
15.0	320

Example on Thomas Method

- Solution
- 1. Plot Measured BOD vs Time as shown on Figure 1; Columns (3) vs (1)

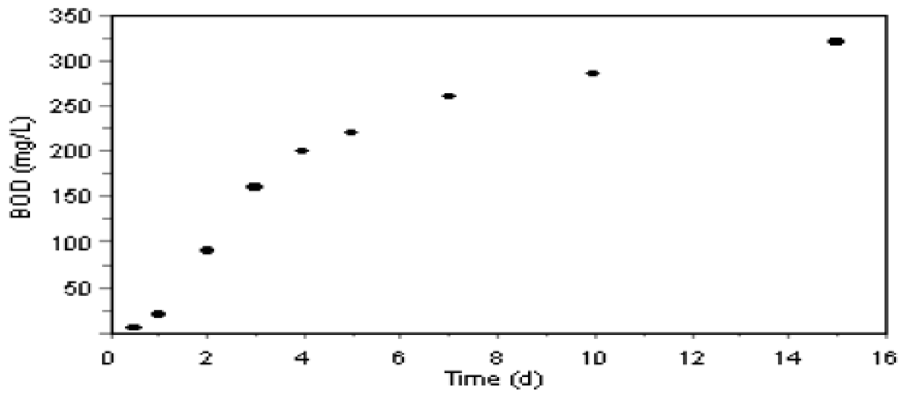


Figure 1: Raw BOD vs Time

Example on Thomas Method

- 2. If **lag time** exists in Figure 1, subtract it from Time (Column 1) to obtain Corrected Time (Column 2).

Time **(1)** d	Corrected Time **(2)** d	Measured BOD **(3)** mg/L	$(t/BOD)^{1/3}$ **(4)**
0.5	....	5	
1.0	0.2	20	0.22
2.0	1.2	90	0.24
3.0	2.2	160	0.24
4.0	3.2	200	0.25
5.0	4.2	220	0.27
7.0	6.2	260	0.29
10.0	9.2	285	0.32
15.0	14.2	320	0.35

Example on Thomas Method

- 3. Calculate Column (4) using Corrected Time and Measured BOD
- 4. Plot Column (4) vs Column (2) as shown in Figure 2

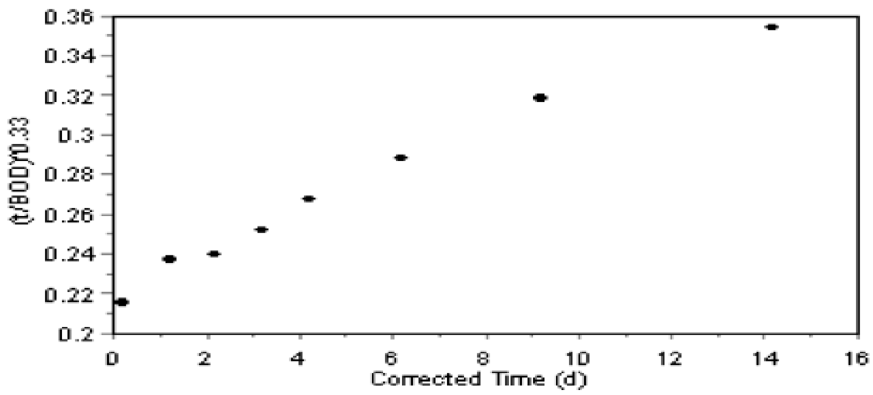


Figure 2: $(t/BOD)^{0.33}$ vs Corrected Time

Example on Thomas Method

- 5. From Figure 2:

  intercept = 0.22 $= (k \cdot BOD_u)^{-\frac{1}{3}}$

  slope = 0.0108 $= \dfrac{k^{\frac{2}{3}}}{6 \cdot BOD_u^{\frac{1}{3}}}$

- 6. Manipulate Slope and Intercept eqns to solve simultaneously for k and BOD_u gives:

  k = 0.295 1/d

  BOD_u = 319 mg/L

Example on Thomas Method

- 7. Using the above coefficients gives the governing BODt equation,

$$BOD_t = 319[1 - e^{-0.295(t-0.8)}]$$

typical values for k and BOD_u for default temperature of 20°C

water type	k, 1/d	BOD_u, mg/L
tap water	<0.1	0 - 1
surface waters	0.1 - 0.23	1 - 30
weak municipal wastewater	0.35	150
strong municipal wastewater	0.4	250
treated effluent	0.12 - 0.23	10 - 30

Effect of Temperature on k (BOD rxn rate constant)

- Temperature strongly influences reaction rate; higher the temp, greater the decay
- Temperature changes are accounted for using the van't Hoff-Arrhenius relationship.

$$k_{T1} = k_{T2} \cdot \theta^{(T1-T2)}$$

$$k_{\mathrm{H},cp}(T) = k_{\mathrm{H},cp}(T^{\ominus}) \exp\left[C\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)\right]$$

where

θ is 1.135 for $4 < T \leq 20°C$

θ is 1.056 for $T > 20°C$

Problem 23.9:

- A wastewater has an estimated 5-day BOD of 160 mg/L. Assuming you were going to use a three-bottle dilution series and 310 mL bottles were used, how many mL of the wastewater would you put in each bottle?

- **Answer:**
- Estimated BOD value falls in **2%** dilution range (see Table 23.11)
- For three-bottle experiment, use one lower and one upper dilution ranges, i.e. **1%** and **5%** together with **2%**.
- Do the rest of the solution for calculating the absolute sample amounts of the respective dilutions in 310 ml volume …

Problem 23.10:

- A wastewater has an estimated 5-day BOD of 300 mg/L. Assuming you were going to use a three-bottle dilution series, what percent mixture of sample would you prepare for adding to each bottle?

- **Answer:**
- Similar way of solution as in problem 23.9…

Problem 23.18:

- The following data were obtained in the analysis of an industrial waste: After 5 days of incubation at 20°C, the residual dissolved oxygen in blanks was 7.80 mg/L, and in a 0.1 percent dilution of the waste was 2.80 mg/L.
- *(a) What is the 5-day BOD of the waste?*
- *(b) How many pounds of 5-day BOD are contained in 10,000 gallons of the waste?*

- ***Answer.***
- (a) Use simplified Eqn (23.14) in the text to calculate the BOD_5 value.

$$BOD_5\ (mg/L) = \frac{B_2 - D_2}{P} \qquad \text{(simplified equation for most uses)} \qquad (23.14)$$

- Please read the explanation for the simplified eqn…
- Result is (7.8-2.8)/(0.1/100)=5000 mg/L BOD_5

- (b) 1 gallon=3.785 L 10000gal=37850 L
- 1 L waste contains 5 g of BOD_5. So, 37850 L waste contains (5gr/L*37850L) = 189250 g = 417 pound of BOD_5 for 10000 gal of waste.

Problem 23.19:

- Determine the 10-day carbonaceous BOD of a river sample from the following data (assume no dilution used).

Analysis, mg/L	Day 0	Day 10
DO	8.3	1.4
NH_3-N	2.1	0.8
NO_2^--N	0.0	0.1
NO_3^--N	0.5	2.1

- The formula weight for each nitrogen species is taken as 14 here since the values are reported as nitrogen, not as the respective ammonia, nitrite, or nitrate

- **Answer 23.19:**
- Before studying the answer, you need to understand the solutions of Examples 23.1 and 23.3. Then study the following solution…

- Total 10-day BOD is (8.3-1.4)=6.9 mg/L.
- This total BOD contains <u>Carbonaceous and Nitrogeneous</u> oxygen demand.
- Nitrogeneous oxygen demand should be calculated separately and subtracted from the total above.

- Lets examine the data given in the Table:

- Total oxidized NH_3-N is 2.1-0.8 = 1.3 mg/L,
- Oxidation to NO_2-N is 0.1 mg/L
- Oxidation to NO_3-N is 2.1-0.5 = 1.6 mg/L
- Ammonia nitrogen (NH_3-N) which was formed during BOD test is 1.6+0.1-1.3 = 0.4 mg/L

- Total nitrogeneous oxygen demand is the sum of
  - the oxidation to nitrite (Eqn. 23.7) and
  - the oxidation to nitrate (Eqn. 23.8):

- **Oxidation to nitrite:**

$$2NH_3 + 3O_2 \xrightarrow{\text{nitrite-forming bacteria}} 2NO_2^- + 2H^+ + 2H_2O$$

3*32 g Oxygen 2*46 g NO_2

- For the formation of 92 g NO_2, 96 g oxygen is needed;
- For 0.33 mg/L NO_2 (0.1 mg/L NO_2-N), **0.34 mg/L oxygen (BOD)** is needed

- **Oxidation to nitrate:**

$$2NO_2^- + O_2 \xrightarrow{\text{nitrite-forming bacteria}} 2NO_3^-$$

32 g Oxygen   2*62 g NO_3

- For the formation of 124 g NO_3, 32 g oxygen is needed;
- For 7.1 mg/L NO_3 (1.6 mg/L NO_3-N), **1.83 mg/L oxygen (BOD)** is needed.

- Then,
- **Total Nitrogeneous BOD** = 0.34+1.83 = **2.17 mg/L**

- **Carbonaceous BOD = Total BOD – Nitrogeneous BOD**
- **= 6.9 - 2.17 = 4.73 mg/L**

Problem 23.20:

- Determine the 12-day carbonaceous BOD of a river sample from the following data in which the diluted sample mixture contained 10 percent of sample.

Analysis, mg/L	Day 0	Day 12
Blank	8.2	8.1
Diluted sample		
DO	8.0	1.4
NH_3-N	1.1	0.6
NO_2^--N	0.0	0.0
NO_3^--N	0.2	1.1

- The formula weight for each nitrogen species is taken as 14 here since the values are reported as nitrogen, not as the respective ammonia, nitrite, or nitrate.
- **Answer:**
- Re-examine the solutions of 23.18 and 23.19 for the solution of this problem…

Problem 23.21:

- In Probs. 23.19 and 23.20, the summation of the inorganic nitrogen species shown at the end of incubation are higher than at day 0. Explain why this might occur.

- **Answer:**
- The answer is in the solution of Problem 23.18. Re-examine the steps of that solution……

TOC

- TOC is the Total Organic Carbon, i.e., the Carbon content of organic materials.

- An Example:
  - C_6H_5OH + 7 O_2 → 6 CO_2 + 3 H_2O
  - 94 gr 224 gr
  - 94 mg/L 224 mg/L ThOD
  - 300 mg/L **715 mg/L Theoretical COD or ThOD**

- **TOC is the amount of Carbon only**. i.e.
- TOC : 6*12= 72 mg/L for 94 mg/L phenol
- For 300 mg/L phenol → ThOD = Th COD = 715 mg/L
- For 300 mg/L phenol → TOC = 300*(72/94) = 229.8 mg/L