

**The Islamic University of Gaza
Faculty of Engineering
Civil Engineering Department**

**Environmental Engineering
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Water Chemistry

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Approaches in Environmental Chemistry

Chemistry is the study of the composition, reactions, and characteristics of matter. It is important because the ultimate fate of many chemicals discharged to air, water, soil, and treatment facilities is controlled by their reactivity and chemical speciation.

Design, construction, and operation of treatment processes thus depend on fundamental chemical processes.

Approaches in Environmental Chemistry

Two very different approaches are used in evaluating a chemical's fate and treatment: kinetics and equilibrium. Kinetics deals with the rates of reactions, and equilibrium deals with the final result or stopping place of reactions. The kinetic approach is appropriate when the reaction is slow relative to our time frame or when we are interested in the rate of change of concentration. The equilibrium approach is useful whenever reactions are very fast, whenever we want to know in which direction a reaction will go, or whenever we want to know the final, stable conditions that will exist at equilibrium.

Activity and Concentration

For a substance dissolved in a solvent, the activity can be thought of as the effective or apparent concentration, or that portion of the true mole based concentration of a species that participates in a chemical reaction, normalized to the standard state concentration. In many environmental situations, activity and concentration are used interchangeably. Places where they begin to greatly differ include seawater, briny groundwater, recycled streams, and highly concentrated waste streams. Activity typically is designated by { } brackets, and concentration by [] brackets.

Activity and Concentration

The ionic strength of a solution (referred to as I or μ) has units of moles/liter and is a measure of the long-range electrostatic interactions in that solution. Ionic strength can be calculated as follows:

$$\mu = 1/2 \sum_i C_i z_i^2$$

where C is the molar concentration of an ionic species i in solution and Z_i is the charge of the ion.

Fortunately, it can be correlated to easily measured water-quality parameters such as total dissolved solids (TDS) or specific conductance:

Activity and Concentration

$$\mu = 2.5 \times 10^{-5} (\text{TDS})$$

where TDS is in mg/L

example/ 3.1 Calculating Ionic Strength and Activity Coefficients for Electrolytes

Calculate the ionic strength and all the individual activity coefficients for a 1 L solution of water at 15°C in which 0.01 mole of FeCl_3 and 0.005 mole of H_2SO_4 are dissolved.

solution

After the two compounds are placed in water, they will completely dissociate to form 0.01 M Fe^{3+} , 0.01 M H^+ , 0.03 M Cl^- , and 0.005 M SO_4^{2-} . The ionic strength is calculated by Equation 3.1:

$$\mu = 1/2[0.01(3+)^2 + 0.01(1+)^2 + 0.03(1-)^2 + 0.005(2-)^2] = 0.075 \text{ M}$$

This ionic strength is relatively high but still much less than that of seawater. The Güntelberg approximation (see Figure 3.1) is useful for calculating activity coefficients for electrolytes when $\mu < 0.1 \text{ M}$.

Acid–Base Chemistry

Acid–base chemistry is important in treatment of pollution and in understanding the fate and toxicity of chemicals discharged to the environment.

pH

$$\text{pH} = -\log[\text{H}^+]$$



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

Acid–Base Chemistry

Table / 3.4

Dissociation Constant for Water at Various Temperatures and Resulting pH of a Neutral Solution

Temperature (°C)	K_w	pH of Neutral Solution
0	0.12×10^{-14}	7.47
15	0.45×10^{-14}	7.18
20	0.68×10^{-14}	7.08
25	1.01×10^{-14}	7.00
30	1.47×10^{-14}	6.92

Acid–Base Chemistry

DEFINITION OF ACIDS AND BASES AND THEIR EQUILIBRIUM CONSTANTS



Table / 3.5

Common Acids and Bases and Their Equilibrium Constants When Added to Water at 25°C

Acids			Bases		
	Name	$\text{p}K_{\text{a}} = -\log K_{\text{a}}$		Name	$\text{p}K_{\text{b}} = -\log K_{\text{b}}$
HCl	Hydrochloric	−3	Cl^-	Chloride ion	17
H_2SO_4	Sulfuric	−3	HSO_4^-	Bisulfate ion	17
HNO_3	Nitric	−1	NO_3^-	Nitrate ion	15
HSO_4^-	Bisulfate	1.9	SO_4^{2-}	Sulfate ion	12.1
H_3PO_4	Phosphoric	2.1	H_2PO_4^-	Dihydrogen phosphate	11.9
CH_3COOH	Acetic	4.7	CH_3COO^-	Acetate ion	9.3
H_2CO_3^*	Carbon dioxide and carbonic acid	6.3	HCO_3^-	Bicarbonate	7.7
H_2S	Hydrogen sulfide	7.1	HS^-	Bisulfide	6.9
H_2PO_4^-	Dihydrogen phosphate	7.2	HPO_4^{2-}	Monohydrogen phosphate	6.8
HCN	Hydrocyanic	9.2	CN^-	Cyanide ion	4.8
NH_4^+	Ammonium ion	9.3	NH_3	Ammonia	4.7
HCO_3^-	Bicarbonate	10.3	CO_3^{2-}	Carbonate	3.7
HPO_4^{2-}	Monohydrogen phosphate	12.3	PO_4^{3-}	Phosphate	1.7
NH_3	Ammonia	23	NH_2^-	Amide	−9

$$K_{\text{a}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Acid–Base Chemistry

example/ 3.6 Acid–Base Equilibrium

What percentage of total ammonia (that is, $\text{NH}_3 + \text{NH}_4^+$) is present as NH_3 at a pH of 7? The pK_a for NH_4^+ is 9.3; therefore,

$$K_a = 10^{-9.3} = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

solution

The problem is requesting

$$\frac{[\text{NH}_3]}{([\text{NH}_4^+] + [\text{NH}_3])} \times 100\%$$

Solving this problem requires another independent equation because the preceding expression has two unknowns. The equilibrium expression for the $\text{NH}_4^+/\text{NH}_3$ system provides the second required equation:

$$10^{-9.3} = \frac{[\text{NH}_3] \times [\text{H}^+]}{[\text{NH}_4^+]} = \frac{[\text{NH}_3] \times [10^{-7}]}{[\text{NH}_4^+]}$$

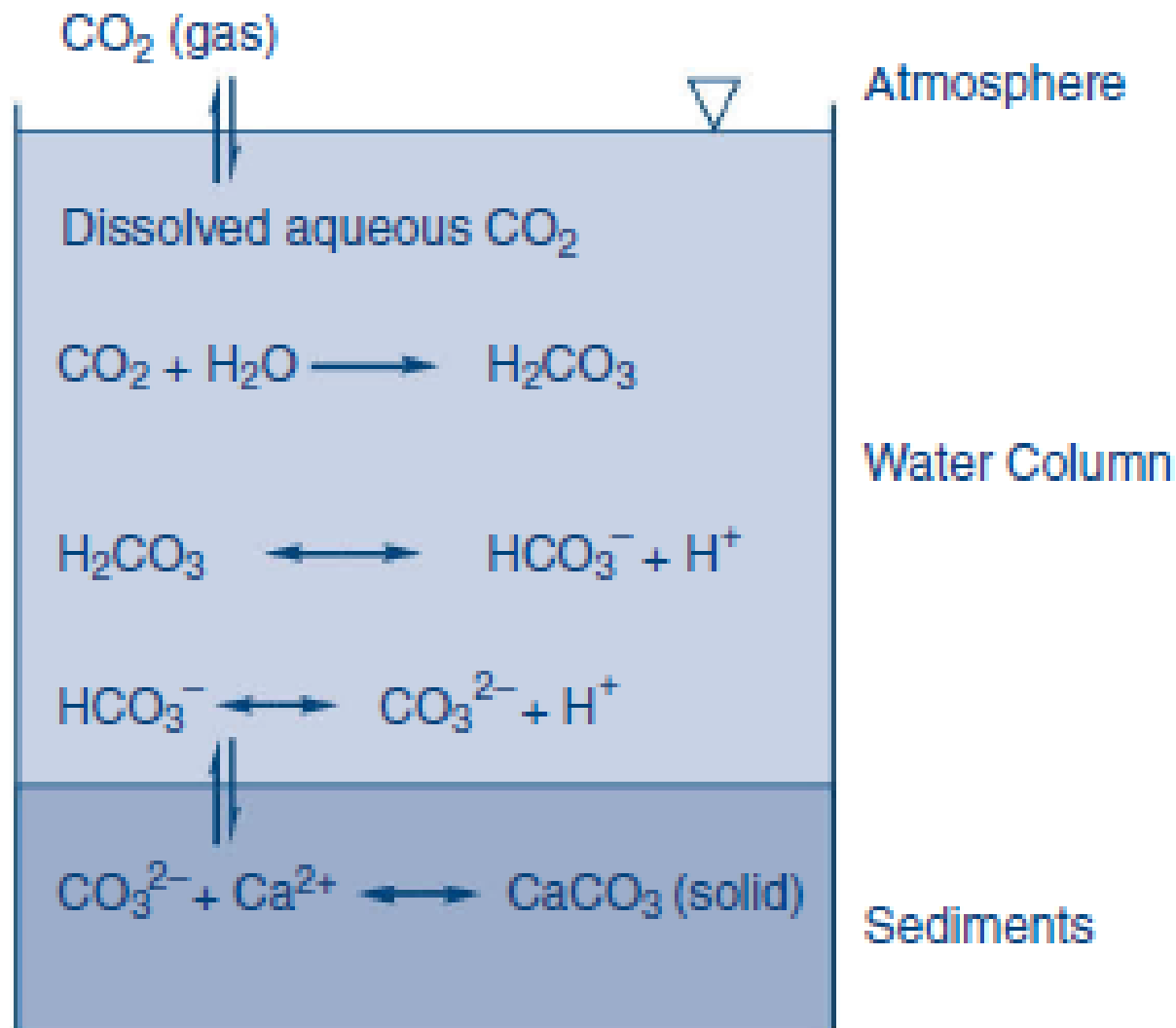
Thus, at $\text{pH} = 7$, $[\text{NH}_4^+] = 200 \times [\text{NH}_3]$. This expression can be substituted into the first expression, yielding

$$\frac{[\text{NH}_3]}{(200 \times [\text{NH}_3] + [\text{NH}_3])} \times 100\% = 0.5\%$$

At this neutral pH, almost all of the total ammonia of a system exists as ammonium ion (NH_4^+). In fact, only 0.5 percent exists as NH_3 !

The form of total ammonia most toxic to aquatic life is NH_3 . It is toxic to several fish species at concentrations above 0.2 mg/L. Thus, wastewater discharges with a pH less than 9 will have most of the total ammonia in the less toxic NH_4^+ form. This is one reason why some wastewater discharge permits for ammonia specify that the pH of the discharge must also be less than 9.

CARBONATE SYSTEM, ALKALINITY, AND BUFFERING CAPACITY



CARBONATE SYSTEM, ALKALINITY, AND BUFFERING CAPACITY



$$\text{Total inorganic carbon} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

Oxidation–Reduction

Some chemical reactions occur because electrons are transferred between different chemical species. These reactions are called oxidation– reduction or redox reactions. Oxidation–reduction reactions control the fate and speciation of many metals and organic pollutants in natural environments, and numerous treatment processes employ redox chemistry.

Oxidation–Reduction

Table / 3.7

Conventions for Assigning Oxidation State to Common Atoms (H, O, N, S) in Molecules

1. The overall charge on a molecule = Σ charges (oxidation state) of its individual atoms.
2. The atoms in the molecule of concern have the following oxidation state; however, these numbers should be set equal to other numbers in reverse order (apply a different number to S before applying N, and so on) such that Convention 1 is always satisfied.

Atom	Oxidation State
H ⁺	+1
O	−2
N	−3
S	−2

Oxidation–Reduction

example/ 3.8 Determining Oxidation States

Determine the oxidation states of sulfur in sulfate (SO_4^{2-}) and bisulfide (HS^-).

solution

We expect the sulfur in sulfate to be more highly oxidized (due to the presence of oxygen in the molecule) than in bisulfide (due to the presence of hydrogen). The overall charge of -2 on sulfate must be maintained, and since the charge on each oxygen atom is -2 (see Table 3.7), the charge on the sulfur in sulfate must be $-2 - 4(-2) = +6$. To maintain the overall charge of -1 on bisulfide, the charge on sulfur must be $-1 - (+1) = -2$. Here the charge on H^+ was $+1$ (see Table 3.7). As expected, the sulfur found in sulfate is more oxidized than sulfur in bisulfide.

Precipitation–Dissolution



$$K_{sp} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{CaCO}_{3(s)}]} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

Precipitation–Dissolution

Table / 3.8

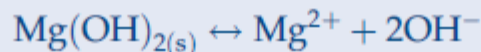
Common Precipitation–Dissolution Reactions, the Associated Solubility Product K_{sp} , and Significance

Equilibrium Equation	K_{sp} at 25°C	Significance
$\text{CaCO}_{3(s)} \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$	3.3×10^{-9}	Hardness removal, scaling, ocean sequestration of carbon dioxide
$\text{MgCO}_{3(s)} \leftrightarrow \text{Mg}^{2+} + \text{CO}_3^{2-}$	3.5×10^{-5}	Hardness removal, scaling
$\text{Ca(OH)}_{2(s)} \leftrightarrow \text{Ca}^{2+} + 2\text{OH}^-$	6.3×10^{-6}	Hardness removal
$\text{Mg(OH)}_{2(s)} \leftrightarrow \text{Mg}^{2+} + 2\text{OH}^-$	6.9×10^{-12}	Hardness removal
$\text{Cu(OH)}_{2(s)} \leftrightarrow \text{Cu}^{2+} + 2\text{OH}^-$	7.8×10^{-20}	Heavy-metal removal
$\text{Zn(OH)}_{2(s)} \leftrightarrow \text{Zn}^{2+} + 2\text{OH}^-$	3.2×10^{-16}	Heavy-metal removal
$\text{Al(OH)}_{3(s)} \leftrightarrow \text{Al}^{3+} + 3\text{OH}^-$	6.3×10^{-32}	Coagulation
$\text{Fe(OH)}_{3(s)} \leftrightarrow \text{Fe}^{3+} + 3\text{OH}^-$	6×10^{-38}	Coagulation, iron removal
$\text{CaSO}_{4(s)} \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$	4.4×10^{-5}	Flue gas desulfurization
$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}_{(s)} \leftrightarrow \text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O}$	$5.5 \times 10^{-14} - 2.5 \times 10^{-13}$	Struvite precipitation for recovery of phosphorus from urine at wastewater treatment plant, struvite precipitation in waterless urinals

Precipitation–Dissolution

example/ 3.9 Precipitation–Dissolution Equilibrium

What pH is required to reduce a high concentration of dissolved Mg^{2+} to 43 mg/L? K_{sp} for the following reaction is $10^{-11.16}$.



solution

In this situation, the dissolved magnesium is removed from solution as a hydroxide precipitate. First, the concentration of Mg^{2+} is converted from mg/L to moles/L:

$$[\text{Mg}^{2+}] = \frac{43 \text{ mg}}{\text{L}} \times \frac{\text{g}}{1,000 \text{ mg}} \times \frac{1 \text{ mole}}{24 \text{ g}} = 0.0018 \text{ M}$$

Then, the equilibrium relationship is written as

$$10^{-11.16} = \frac{[\text{Mg}^{2+}] \times [\text{OH}^{-}]^2}{[\text{Mg}(\text{OH})_{2(s)}]}$$

Substituting values for all the known parameters,

$$10^{-11.16} = \frac{[0.0018] \times [\text{OH}^{-}]^2}{1}$$

Solve for $[\text{OH}^{-}] = 6.2 \times 10^{-5} \text{ M}$. This results in $[\text{H}^{+}] = 10^{-9.79} \text{ M}$, so $\text{pH} = 9.79$. At this pH, any magnesium in excess of 0.0018 M will precipitate as $\text{Mg}(\text{OH})_{2(s)}$ because the solubility of Mg^{2+} will be exceeded.

ORGANICS

• Biodegradable Organics

Biodegradable materials consists organics that can be utilized for food by naturally occurring microorganisms within a reasonable length of time.

Source of organics

- Organics include fats, proteins, alcohols, acids, aldehydes, and esters.
- Organics are the end product of the initial microbial decomposition of plant or animal tissue.
- Result from domestic or industrial wastewater discharge.

Microbial utilization of dissolved organics can be accompanied by *oxidation* (addition of oxygen to elements of the organic molecule) or by *reduction* (addition of hydrogen).

Biochemical Oxygen Demand - BOD, g/m^3

Definition:

Mass of dissolved oxygen consumed in definite time by the aerobic microbial utilization of organics substances.

Measurement (Standard Test):

- 300 mL BOD bottle is used and placed in an air-tight container at 20°C for 5 days.
- Light must be excluded from the bottle to prevent algal growth that may produce oxygen in the bottle.
- Dilution of the sample with BOD-free, oxygen saturated water is necessary to measure BOD values greater than just a few milligrams per litre.

Determination of BOD

The BOD of a diluted sample is calculated by:

$$\text{BOD (mg/L)} = (D_i - D_f)/P$$

- Where:
 - D_i = initial DO in the diluted sample (mg/L)
 - D_f = DO in the diluted sample after incubation (mg/L)
 - P = decimal fraction of wastewater in total volume
= mL wastewater/300mL

BOD Test Range

By using percent mixtures		By direct pipetting into 300-mL bottles	
% mixture	Range of BOD, mg/L	mL	Range of BOD, mg/L
0.01	20,000–70,000	0.02	30,000–105,000
0.02	10,000–35,000	0.05	12,000–42,000
0.05	4,000–14,000	0.10	6,000–21,000
0.1	2,000–7,000	0.20	3,000–10,500
0.2	1,000–3,500	0.50	1,200–4,200
0.5	400–1,400	1.0	600–2,100
1.0	200–700	2.0	300–1,050
2.0	100–350	5.0	120–420
5.0	40–140	10.0	60–210
10.0	20–70	20.0	30–105
20.0	10–35	50.0	12–42
50.0	4–14	100.0	6–21
100.0	0–7	300.0	0–7

Assume an initial DO 9 (mg/L) in the mixture, with a minimum of 2 and a maximum of 7 mg/L of O₂ being consumed.

Example

- The BOD of a wastewater is suspected to range from 50 - 200 mg/L.
 - Three dilutions are prepared to cover this range. The procedure is the same in each case.
1. First the sample is placed in the standard BOD bottle and is then diluted to 300 mL with organic- free, oxygen-saturated water.
 2. The initial dissolved oxygen is determined, and
 3. The bottles tightly stoppered and placed at 20°C for 5 days,

After which the dissolved oxygen is again determined.

wastewater mL	DO ₁ mg/L	DO ₅ mg/L	O ₂ used mg/L	P	BOD ₅ mg/L
5	9.2	6.9	2.3	0.017	138
10	9.1	4.4	4.7	0.033	141
20	8.9	1.5	7.4 (> max.)	0.067	111

The average BOD of the sample = $(138+141)/2 = 140$ mg/L

BOD for any time period can be determined as:

- The rate at which organics are utilized by microorganisms is assumed to be **a first- order reaction**,
- The rate at which organics utilized is proportional to the amount available.

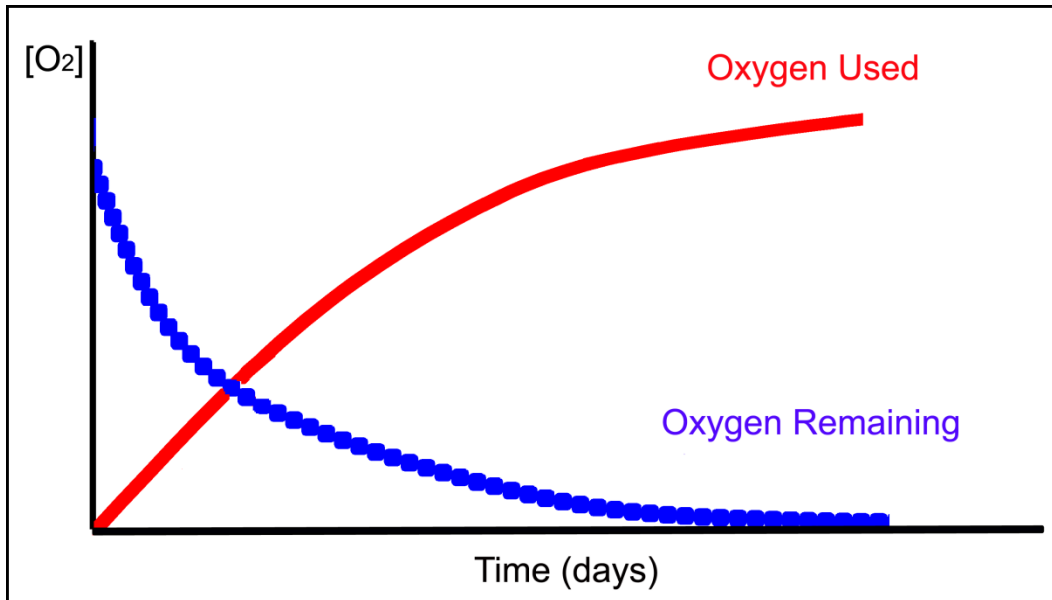
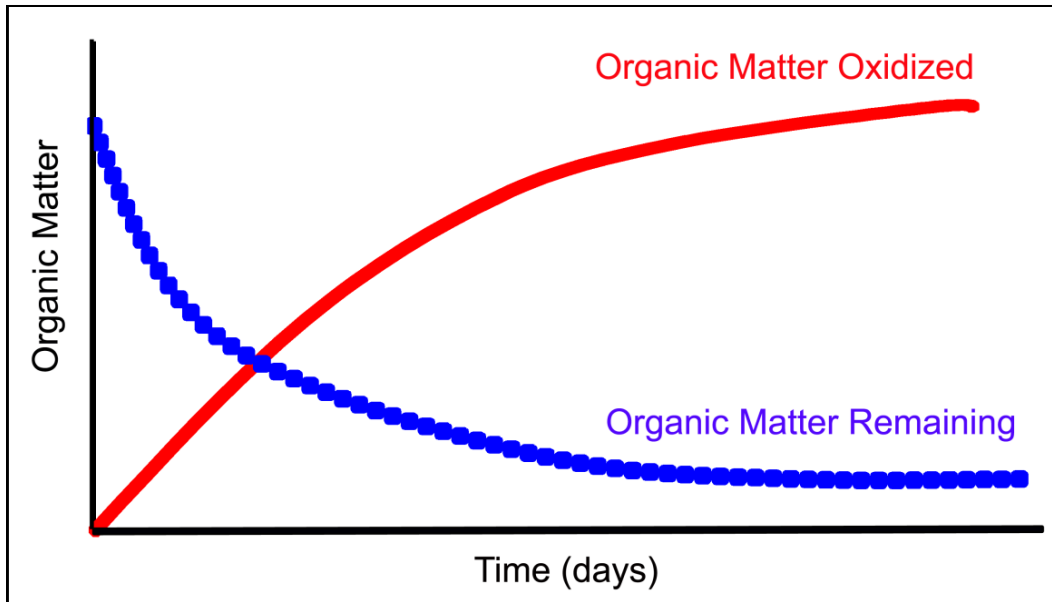
$$\frac{dL_t}{dt} = -k.L_t$$

where:

- L_t is the oxygen equivalent of the organics at time t (mg/L),
- k is the reaction constant (d^{-1})

$$\int_{L_0}^L \frac{dL_t}{L_t} = -k \int_0^t dt \Rightarrow \ln \frac{L_t}{L_0} = -kt \Rightarrow L_t = L_0 e^{-kt}$$

- L_0 is the total oxygen equivalent of the organics at time 0 (mg/L),
- L_t is the oxygen remaining at time t (mg/L),



The amount of oxygen used in the consumption of organics = **BOD** , can be found from the L_t value as the following:

If

- L_o is the total oxygen equivalent of the total mass organics at time 0 (mg/L),
- L_t is the oxygen remaining at time t (mg/L),

$$Y_t = L_o - L_t = L_o - L_o e^{-kt} \Rightarrow Y_t = L_o (1 - e^{-kt})$$

Y_t represents the **BOD_t** of the water

Note:

BOD (ultimate) = the initial oxygen equivalent of the water L_o

K constant

- The value of k determines the speed of the BOD reaction.
- K values range from $(0.1-0.5) \text{ d}^{-1}$ depending on the nature of the organic molecules.
- K value for any given organic compound is temperature-dependent, because microorganisms are more active at higher temperatures. **(k increase with increasing temperatures).**

$$k_T = k_{20} \theta^{(T-20)}$$

$$\theta = 1.047$$

Example

The BOD_5 of a wastewater is determined to be 150 mg/L at 20°C.

The k value is known to be 0.23 per day.

What would the BOD_8 be if the test were run at 15°C?

Solution:

$$BOD_t = L_o(1 - e^{-kt}) \Rightarrow BOD_5 = L_o(1 - e^{-kt})$$

$$150 = L_o(1 - e^{-0.23 \times 5}) \Rightarrow L_o = \frac{150}{1 - e^{-0.23 \times 5}} = 220 \text{ mg / L}$$

$$k_T = k_{20} \theta^{(T-20)} \Rightarrow k_{15} = k_{20} \times 1.047^{(15-20)} = 0.18$$

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

$$BOD_8 = 220(1 - e^{-0.18 \times 8}) = 168 \text{ mg / L}$$

Example

200 mL of a river water was collected. 2-mL of river water diluted to 1 L, aerated and seeded. The dissolved oxygen content was 7.8 mg/L initially. After 5 days, the dissolved oxygen content had dropped to 5.9 mg/L. After 20 days, the dissolved oxygen content had dropped to 5.3 mg/L. What is the ultimate BOD?

Solution

$$\text{BOD}_5 = \frac{7.8 \text{ mg/L} - 5.9 \text{ mg/L}}{2 \text{ mL}/1000 \text{ mL}} = 950 \text{ mg/L}$$

$$\text{BOD}_{20} = \frac{7.8 \text{ mg/L} - 5.3 \text{ mg/L}}{2 \text{ mL}/1000 \text{ mL}} = 1250 \text{ mg/L}$$

$$\underline{\text{BOD}_5} = \underline{(1 - e^{-k(5 \text{ days})})}$$

$$\text{BOD}_{20} \quad (1 - e^{-k(20 \text{ days})})$$

$$\underline{950} = \underline{(1 - e^{-k(5 \text{ days})})}$$

$$1250 \quad (1 - e^{-k(20 \text{ days})})$$

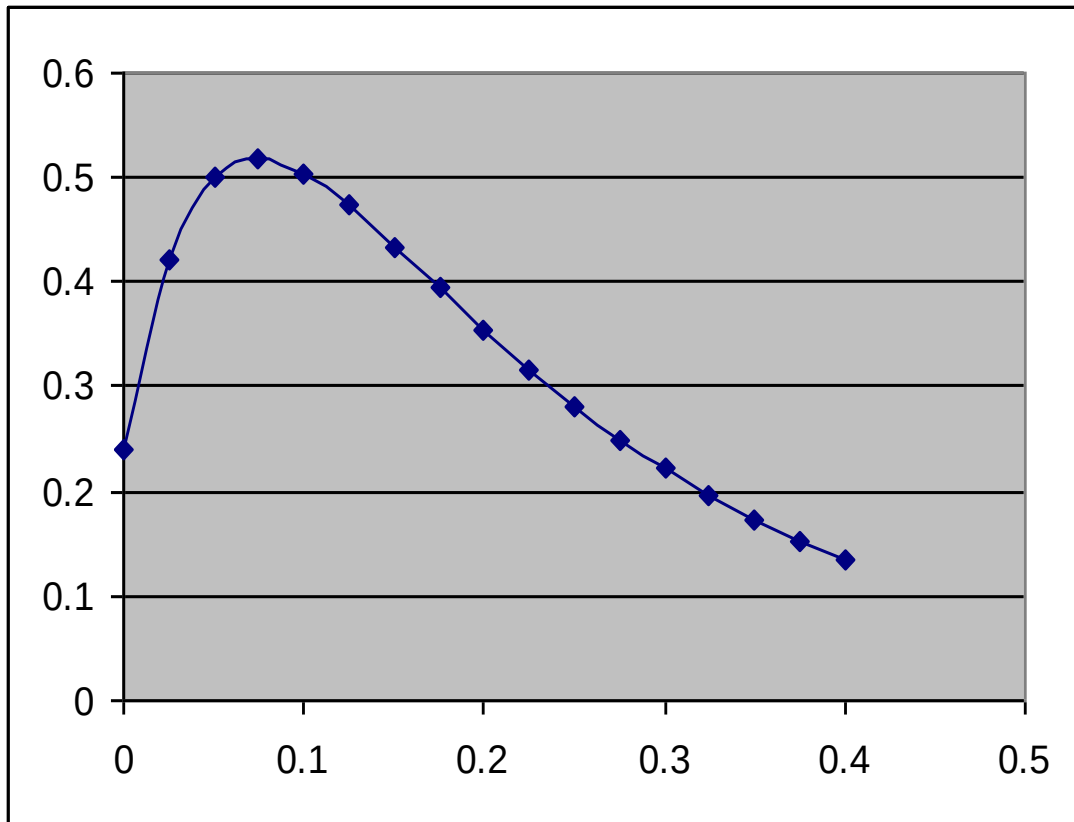
$$0.76 = \frac{(1 - e^{-k(5 \text{ days})})}{(1 - e^{-k(20 \text{ days})})}$$

$$0.76 = \frac{(1 - e^{-k(5 \text{ days})})}{(1 - e^{-k(20 \text{ days})})}$$

$$0.76 - 0.76 e^{-k(20)} = 1 - e^{-k(5)}$$

$$e^{-k(5)} - 0.76 e^{-k(20)} = 1 - 0.76 = 0.24$$

We just graph the left side as a function of k and look to see where it equals 0.24 (or you can use solver on your calculator)



k	$e^{-5k} - 0.76e^{20k}$
0	0.24
0.025	0.421534
0.05	0.499212
0.075	0.51771
0.1	0.503676
0.125	0.472877
0.15	0.434528
0.175	0.393912
0.2	0.35396
0.225	0.31621
0.25	0.281384
0.275	0.249734
0.3	0.221246
0.325	0.195769
0.35	0.173081
0.375	0.152935
0.4	0.13508

The k value is...

0.28 day⁻¹

$$\text{BOD}_5 = \text{BOD} (1 - e^{-k(5 \text{ days})})$$

$$950 \text{ mg/L} = \text{BOD} (1 - e^{-(0.28)(5)})$$

$$\text{BOD} = 1261 \text{ mg/L}$$

Notes

- The water body is considered to be very clean if its BOD_5 at 20°C is less than 1 mg/litre (i.e. ppm).
- The water body is considered poor if its BOD_5 at 20°C is more than 5 mg/litre.
- The BOD_5 estimate however excludes complex organics such as cellulose, and proteins, which cannot be readily biodegraded by bacteria.

Non-biodegradable Organics

- Some organic materials are resistant to biological degradation (e. g. cellulose, phenols, acids, proteins, benzene, ...etc)
- Some organics are non-biodegradable because they are toxic to organisms (i.e pesticides).
- Measurement of non-biodegradable organics is usually by **chemical oxygen demand (COD)** test, also by **total organic carbon (TOC)**

COD & TOC

1. Chemical Oxygen Demand (COD):

- One problem with the BOD test is that it takes *5 days to run, if the organic compounds* were oxidized chemically instead of biologically, the test could be shortened considerably.
- Such oxidation can be accomplished with the chemical oxygen demand (COD) test.
- Since the BOD measurement includes only the readily biodegradable organics that are decomposed aerobically by simple bacteria, we use the chemical oxygen demand (COD) measurement to indicate the amount of oxidizable material present in the effluent sample that can be oxidised by a strong chemical oxidant.

- COD results are always higher than BOD results.
- **One example** of this is wood pulping waste, in which compounds such as **cellulose** are easily oxidized chemically (high COD) but are very slow to decompose biologically (low BOD).
- The standard COD test uses a mixture of potassium dichromate and sulfuric acid to oxidize the organic matter (HCOH), with silver (Ag^+) added as a catalyst.

2. Total Organic Carbon (TOC):

- **TOC = Carbon mass of the organic substances in water/wastewater**
- Total organic carbon is measured by oxidizing the organic carbon to CO_2 and H_2O and measuring the CO_2 gas using an infrared carbon analyzer.

Nutrients

- **Nutrients** are elements essential to the growth and reproduction of plants and animals and aquatic species.
- Include carbon, nitrogen, and phosphorus.
- Nitrogen and phosphorus are **the main nutrients** in aquatic plant growth.

Carbon

- Source: carbon dioxide from the atmosphere, alkalinity, decay product of organics.

Nitrogen

Source

Nitrogen occurs in five major forms in aquatic environments: organic nitrogen, ammonia, nitrite, nitrate, and dissolved nitrogen gas

1. Nitrogen gas (N_2) is the primary component of the earth's atmosphere and is extremely stable. N_2 Reacts with O_2 to form nitrogen oxides.
2. Nitrogen is a constituent of proteins and chlorophyll. Decay of plants and animals (organics), proteins are converted to amino acids and reduced to ammonia (NH_3), which may oxidized to nitrate (NO_2^-) and then to (NO_3^-) in the presence of oxygen.
3. Animal wastes chemical fertilizers and wastewater discharge may discharged to streams or enter groundwater .
4. Nitrogen compounds can be oxidized to NO_3^- by soil bacteria and may carried out into GW by percolating water.

Impact

- Nitrate can cause serious problems and even death to infant animals and humans.
- Nitrate poisoning has been referred to as “blue baby” syndrome or “methemoglobinemia”

Measurement

- Test for nitrogen forms in water include analysis for ammonia (NH_3 , NH_4^+), nitrate, and organic nitrogen, expressed as mg/L as nitrogen.
- Wastewater and polluted water: NH_4^+ and organic nitrogen analysis.
- Clean water and treated wastewater: nitrate test

Phosphorus

Source

- phosphorus occurs almost as phosphate (PO_4^{3-})
- May be soluble or particulate form or may be constituents of plants or animal tissue.
- Constituents of soils , used extensively in fertilizers.
- Constituents of animal waste and municipal wastewater.
- Industrial waste.

Impact

- The tendency for phosphate to adsorb to soil particles limits its movement in soil moisture and groundwater.
- Not toxic and do not represent a direct health threat to human and other organisms.
- But, it represent indirect threat to water quality (surface water; the growth of algae in most lakes is limited by the availability of phosphorus, if phosphorus is in sufficient supply, nitrogen is usually the next limiting ***nutrient***).

Measurement

- mg/L phosphate as phosphorus.