L_0 is called the ***ultimate BOD*'** (**BOD_{ult}**), because it is the BOD that would be exerted if the organic degraded completely.

Example. What is the ultimate BOD of the solution containing 15 mg/L C_4H_7ON that was considered previously?

$$\left(15\frac{\text{mg } C_4H_7ON}{\text{L}}\right)\left(\frac{1 \text{ mol } C_4H_7ON}{85,000 \text{ mg } C_4H_7ON}\right)\left(\frac{4.5 \text{ mol } O_2}{\text{mol } C_4H_7ON}\right)\left(\frac{32,000 \text{ mg}}{\text{mol C}}\right)$$

$$= 25.4\frac{\text{mg } O_2}{\text{L}} = 25.4\frac{\text{mg BOD}}{\text{L}}$$

Example. A solution with L_o = 400 mg/L and k_1^* = 0.1/d is incubated for five days Find L_5 and y_5. (Note: k_1^* is same as k_1, but for base 10.)

$$L_5 = L_o\left(10^{-k_1^* t}\right) = \left(400 \text{ mg/L}\right)10^{-0.5} = 126 \text{ mg/L}$$

$$y_5 = L_o - L_5 = \left(400 - 126\right)\text{mg/L} = 274 \text{ mg/L}$$

How much O_2 is consumed between days 5 and 10?

$$y_{10} = L_o\left(1 - 10^{-k_1^*(10)}\right) = 360 \text{ mg/L}$$

$$y_{5\to10} = y_{10} - y_5 = \left(360 - 274\right)\text{mg/L} = 86 \text{ mg/L}$$

The BOD Test: Concept and Key Features

- *[Biodeg. Organics] hard to quantify directly*
- *Easier to quantify O_2 in solution, and compute O_2 that has been consumed (by difference with $O_{2,init}$)*
- *O_2 that has been consumed when reaction is complete indicates [Biodeg. Organics] that were present initially*
- *Both L (BOD remaining) and y (BOD exerted) are commonly called just the 'BOD', in which case the meaning has to be understood from context*

- *L is commonly referred to as though it represents the concentration of degradable organic matter (which it is, indirectly). But it is actually measured and reported as a concentration of O_2 (either potential O_2 consumption remaining [L] or O_2 consumption that has actually occurred [y])*
- *Might take long time for reaction to be complete, so partial reaction is analyzed (typically, for 5 d), and first-order rate model is used to predict ultimate amount of reaction*
- *Conditions during test must not impede reaction progress*
  - *[O_2] (i.e., DO) must be sufficient throughout (dilute if L_0 too large)*
  - *Essential nutrients must be present (add if needed)*
  - *Appropriate organisms must be present (inoculate)*

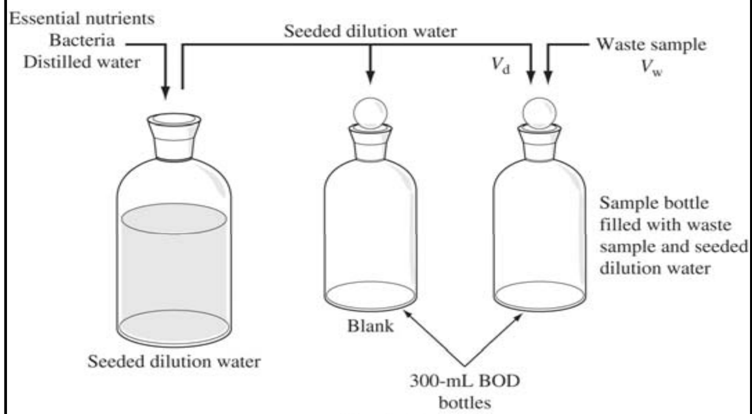

Figure: 05-09

Alternative Indicators of Oxygen Demand

- *Oxygen demand attributed solely to oxidation of carbon is called 'carbonaceous oxygen demand' (CBOD)*
- *Some oxygen can be demanded by inorganic species (e.g., Fe^{2+}, Mn^{2+}, HS^{-}), BOD_{inorg}.*
- *If a BOD test is carried out for a long time (>10 d) or if 'nitrifying' organisms are present in the feed, NH_4^+ can be oxidized to nitrate (NO_3^-), exerting 'nitrogenous oxygen demand' (NOD).*

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

BOD and DO in Streams

- *Assuming a river has plug flow, dynamics of organic decay (L vs t) are similar to those in BOD test – first order reaction. k might be different because of organism population or T*

$$r_L = r_{O_2\ \text{depletion}} = -k_d L$$

- *Unlike in BOD test, O_2 can be replenished (from the air):*

$$\underset{(\text{"reaeration"})}{r_{O_2\ \text{entry}}} = k_r\left(O_{2,eq} - O_2\right) = k_d\left(\text{"}O_2\ \text{deficit"}\right) = k_d D$$

- *Assuming PFR behavior, O_2 depletion and reaeration over distance are same as in a batch system, so:*

$$r_{O_2\ \text{net}} = \frac{d[O_2]}{dt} = -k_d L + k_r D$$

$D \equiv [O_2] - [O_2]_{eq}$, so $dD = d[O_2]$. Therefore:

$$\frac{dD}{dt} = -k_d L_0 \exp(-k_d t) + k_r D$$

- *Solution of first order ODE yields:*

$$D = \frac{k_d L_0}{k_r - k_d}\left(\exp[-k_d t] - \exp[-k_r t]\right) + D_0 \exp[-k_r t]$$

$$t_{crit} = \frac{1}{k_r - k_d} \ln\left\{\frac{k_r}{k_d}\left[1 - \frac{D_0 (k_r - k_d)}{k_d L_0}\right]\right\}$$

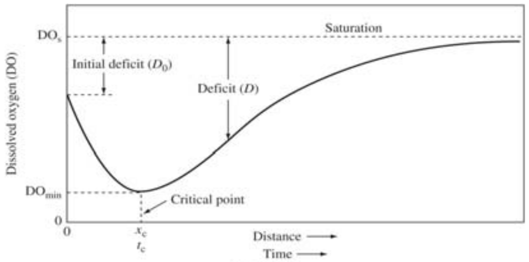

Figure: 05-15

$$\frac{d[O_2]}{dt} = -k_d L + k_r D$$

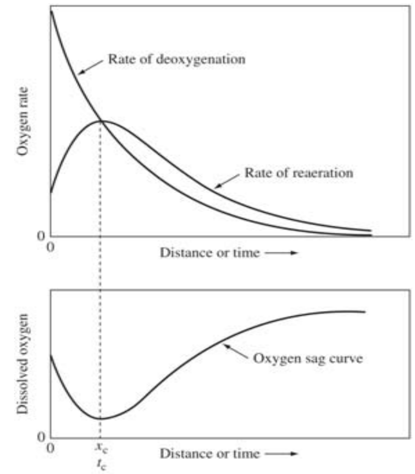

Figure: 05-16

Table 6.2 Stream Reaeration Formulas

O'Connor–Dobbins[9]	$k_a = \frac{12.9u^{0.5}}{H^{1.5}}$		
Owens–Edwards–Gibbs[10]	$k_a = \frac{23u^{0.73}}{H^{1.75}}$	for	$H = 1–2.5$ $\bar{u} = 0.1–0.5$ $Q = 4–36$
Churchill–Elmore–Buckingham (TVA)[11]	$k_a = \frac{11u}{H^{1.67}}$	for	$H = 2–11$ $\bar{u} = 2–5$ $Q = 1000–17{,}000$
USGS	$k_a = \frac{7.6u}{H^{1.33}}$		
Tsivoglou	$k_a = \frac{0.048\,\Delta S}{t}$	for	$Q = 5–3000$

where k_a = reaeration rate constant (base e), day^{-1}
$\bar{u}$ = mean stream velocity, ft sec^{-1}
H = mean stream depth, ft
ΔS = water surface elevation change, ft
Q = flowrate, ft^3 s^{-1}
t = travel time, days

Parameter	Value	θ, Temperature Correction[a]
CBOD deoxygenation, k_d	0.05–0.5 day^{-1}	1.048
CBOD deoxygenation plus sedimentation, k_r	0.5–5 day^{-1}	1.04
NBOD deoxygenation, k_n	0.05–0.5 day^{-1}	1.08
Reaeration, k_a		
Slow, deep rivers	0.1–0.4 day^{-1}	1.024
Typical conditions	0.4–1.5 day^{-1}	1.024
Swift, deep rivers	1.5–4.0 day^{-1}	1.024
Swift, shallow rivers	4.0–10 day^{-1}	1.024
Sediment oxygen demand, S		
Natural to low pollution	0.1–1.0 g m^{-2} d^{-1}	1.065
Moderate to heavy pollution	5–10 g m^{-2} d^{-1}	1.065
Net primary production, $(P - R)$		
Daily average value $(P - R)$	0.5–10 mg L^{-1} d^{-1}	1.066
P_{max}, maximum daily production	2–20 mg L^{-1} d^{-1}	
R, respiration only	1–10 mg L^{-1} d^{-1}	
Background D.O. Deficit, D_b	0.5–2 mg L^{-1}	NA
Coliform bacteria die-away, k		
Freshwater	0.5–5 day^{-1}	1.07
Saltwater	2–40 day^{-1}	1.10
Virus particles in marine waters	0.03–0.16 day^{-1}	1.10

[a] $k_T = k_{20}\,\theta^{(T-20)}$ from Thomann and Mueller.[13]

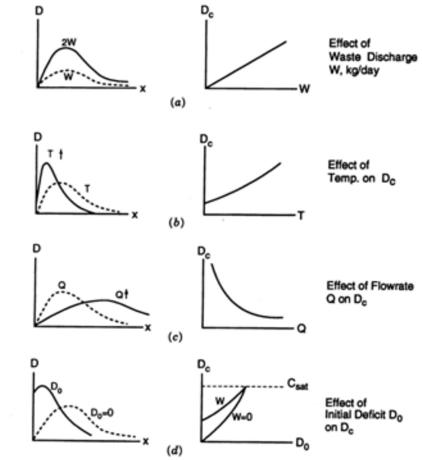

Figure 6.4 Effect of waste discharge (W), temperature (T), flowrate (Q), and initial deficit (D_0) on the critical dissolved oxygen deficit concentration (D_c).

Summary of Key Points

- *Biodegradable organics consume O_2 when they decay aerobically*
- *Amount of O_2 consumed by the organics (y_t), and amount that would be consumed if the remaining organics decayed (L_t), are used to quantify biodegradable organic conc'n*
- *BOD test is a standardized approach for quantifying BOD under favorable conditions for decay*
- *NH_4^+ is often released in early part of BOD test; given enough time, or nitrifying bacteria in the feed, it can subsequently decay, consuming O_2*

Summary of Key Points

- *In rivers (PFRs), organic decay and O_2 consumption follow same pattern as in BOD tests, albeit typically slower*
- *Reaeration from atmosphere proceeds at a rate proportional to the DO deficit, with a rate constant dependent on fluid energy (increases with velocity, decreases with depth) and temperature*
- *Net effect of decay and reaeration leads to a characteristic pattern of DO vs. distance or time, with a minimum DO at a critical x or t*
- *"DO sag" curve is classical example of combination of kinetics (L decay) and equilibrium processes with mass balance concept to derive an important environmental prediction*