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The BOD

Not just my nickname

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What is BOD?

Biochemical Oxygen Demand

It is just what it sounds like, it is the oxygen required by biochemical processes.

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What biochemical processes?

Bacteria

In the normal course of an aquatic ecosystem, there is significant bacterial activity that serves to decompose organic matter under normally aerobic conditions. [Aerobic – requiring oxygen]

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What is BOD, again?

Biochemical Oxygen Demand

The oxygen REQUIRED by biochemical processes to COMPLETELY aerobically decompose organic matter.

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How is BOD different than dissolved oxygen?

BOD isn't really there.

BOD is the amount of oxygen that would be consumed given sufficient time, bacteria and oxygen to completely decompose the organic matter.

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How is BOD different than dissolved oxygen?

"Dissolved oxygen" is there. It is a measure of how much oxygen is dissolved in a water sample. It is a measure of oxygen content.

BOD is the amount of oxygen that would be consumed to completely decompose the organic matter in a water sample. It is not an indication of oxygen content. It is an indication of the amount of organic material present.

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The Reaction

Complete oxidation (combustion) of organic materials yield identical products no matter what the organic starting material.

$$C_nH_aO_bN_c + O_2 \rightarrow CO_2 + H_2O + NH_3$$

(unbalanced)

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The Balanced Equation

$$C_nH_aO_bN_c + (n+a/4 - b/2 - 3c/4) O_2 \rightarrow$$
$$n CO_2 + (a/2 - 3c/2)H_2O + c NH_3$$

Note: Don't get too hung up on the numbers, we don't use the stoichiometry very often.

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How would you determine BOD?

Add bacteria.

Add oxygen quantitatively.

Wait until all of the organic material is gone.

Report on the amount of oxygen used.

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What is the problem with that little scheme?

What bacteria? There are millions of different kinds.

How long? What if it takes 10 years for all the organic material to disappear? What if some of it NEVER decomposes?

Other factors: Temperature? Amount of light present? Concentration of oxygen?

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Solution to the Problem

Standardize the type of bacteria.

Standardize the temperature.

Standardize the amount of oxygen present - saturate it.

Standardize the time - assume the kinetics.

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What's "kinetics" mean?

Kinetics is the rate at which something happens.

Joe's 1st Rule of Chemistry:

Units! Units! Units!

Kinetics has units of...
of events/unit time

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Kinetics in a Chemical sense

In Chemistry, Kinetics usually refers to the "rate" at which a reaction occurs.

In other words, Chemical Kinetics has units of # of reactions/sec or # of moles of reactions/sec.

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Determining Rate

The rate is then calculated by taking the change in concentration divided by the change in time:

$$\frac{\text{final concentration} - \text{initial concentration}}{\text{final time} - \text{initial time}}$$

The rate is always a positive quantity, so you add a negative sign if discussing the rate in terms of one of the reactants that is decreasing.

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Chemical Kinetics

What do you think the rate of a reaction depends upon?

Temperature
Pressure (if a gas is involved)
Concentration of reactants – Why?

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Is the rate of a reaction constant?

Assuming the pressure and temperature are constant, is the rate of a reaction constant?

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Is the rate of a reaction constant?

Imagine a hypothetical reaction:

$$A + 2 B \rightarrow 3 C$$

What happens?

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Is the rate of a reaction constant?

- Eventually, most reactions either:
 - Reach completion
 - Reach equilibrium
- When the concentrations stop changing, the “rate” is zero. So, the rate isn’t usually constant forever, even if it is constant for a certain period of time.

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What does the rate depend upon?

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- Why does a reaction stop?

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What does the rate depend upon?

- Why does a reaction stop?
 - you run out of a reactant (limiting reagent problem)
 - you reach equilibrium

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What does the rate depend upon?

- Why does a reaction stop?
 - you run out of a reactant (limiting reagent problem)
 - you reach equilibrium (equilibrium problem)
- In either case, it is the **concentration** that determines when it stops; you either reach equilibrium concentration, or you use up the total concentration of the limiting reagent.

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Rates MUST depend on concentration!

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Rate laws

So, reaction rates depend on concentration.

Concentration of what?

What is the dependence? Is the dependence linear or super-linear or sub-linear?

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It depends...

There is no universal answer. The rates of different chemical reactions depend on different things. It's a question of molecular dynamics.

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$A + 2 B \rightarrow 3 C$

What does that equation mean?

It means that if you take 1 molecule (or mole) of A and mix it with 2 molecules (or 2 moles) of B, you should end up with 3 molecules (or 3 moles) of C.

Is there only 1 way this can occur?

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$A + 2 B \rightarrow 3 C$

Suppose 2 B molecules collide and form a new molecule "D" in a very slow step and then D jumps on A to create a new molecule E which then falls apart quickly into 3 C molecules:

$B + B \rightarrow D$ very slow
 $D + A \rightarrow E$ very fast
 $E \rightarrow 3 C$ very fast

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$A + 2 B \rightarrow 3 C$

$B + B \rightarrow D$ very slow
 $D + A \rightarrow E$ very fast
 $E \rightarrow 3 C$ very fast

In this case, the rate should be dominated by the first (slow) step. It is the "rate limiting step".
If this were the case, would you expect the concentration of A to matter?

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$A + 2 B \rightarrow 3 C$

$B + B \rightarrow D$ very slow
 $D + A \rightarrow E$ very fast
 $E \rightarrow 3 C$ very fast

In this case, the rate should be dominated by the first (slow) step. It is the "rate limiting step".
If this were the case, would you expect the concentration of A to matter?
Probably not, since it isn't involved in the really slow step.

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The rate limiting step

$A \rightarrow 2 D$ (slow)
 $D + B \rightarrow E$ (fast)
 $E + E \rightarrow 3 C$ (fast)

Since the 1st step is slow, the entire rate may only depend on that step. If so, the overall rate will only depend on the [A] since no B is involved.

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The rate limiting step

A + B → D (slow)
D + B → E (fast)
E → 3 C (fast)

In this case, since the slow step involves both A and B, you might expect the rate to depend on both concentrations.

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The BOD reaction

Now think back to BOD. What's the general reaction:

In the presence of bacteria:

$$C_nH_aO_bN_c + O_2 \rightarrow CO_2 + H_2O + NH_3$$

(the bacteria is not consumed in the reaction, it is a spectator)

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The BOD reaction

$$C_nH_aO_bN_c + O_2 + \text{bacteria} \rightarrow CO_2 + H_2O + NH_3 + \text{bacteria}$$

What COULD this reaction depend on?

[O₂]
[C_nH_aO_bN_c]
[bacteria]
Type of bacteria

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Toooooo Complicated

But we can simplify by standardizing:

We take a specific mix of bacteria that is STANDARD, add a certain amount of oxygen that is STANDARD, and run the test for a given amount of STANDARD time – and then assume “average kinetics”.
