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Dissolved Oxygen

I can't breath in the water – but the fish can!

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Oxygen

Oxygen is one of the fundamental resources required by life forms on Earth.

Aquatic ecosystems have a wide assortment of life forms.

Oxygen is also required for some natural chemical decays.

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What do YOU know about oxygen?

1. Oxygen is a gas at room temperature.
2. Oxygen is a diatomic molecule – $O_{2.}$
3. Oxygen is soluble in water.
4. Oxygen is clear and colorless.
5. Oxygen has no smell.
6. Oxygen is highly reactive.

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It is still all about the water…

So let's focus on oxygen in water.

It's a water-soluble gas.

What issues does that suggest?

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Aqueous oxygen

Solubility is limited.
- In pure water, solubility is only a function of temperature.
- As temperature increases…
  - …solubility decreases.
- As the atmospheric pressure increases…
  - …solubility increases.

What if it isn't "pure" water?

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Aqueous oxygen

"Pure water" means it is only water and nothing but water, it doesn't mean it's clean. So "not-pure water" doesn't mean it is dirty, just that there are other molecules present – whether good or bad.

Does this affect the oxygen?

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Aqueous oxygen

The solubility of all molecules is affected by the presence of other molecules.

Some things increase solubility, most things decrease the solubility.

Not pure water tends to have a LOWER dissolved oxygen concentration.

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β– a measure of impurity

Normal solubility of oxygen in pure water at 1 atm and 25° C is 8 mg/L.

This is a modest value – oxygen is considered to be a poorly soluble gas in water!

Impure water will typically have a value less than 8 mg/L (REMEMBER, it is temperature dependent)

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β– a measure of impurity

The ratio between the actual solubility and the theoretical solubility is β:

$$\beta = \frac{\text{actual mg/L } O_2}{\text{theoretical mg/L } O_2}$$

The smaller β is, the more "impure" the water is.

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Solubility is about equilibrium

Keep in mind that "solubility" is an equilibrium value representing the MAXIMUM amount that can be dissolved.

Equilibrium is not achieved instantaneously – it takes time for oxygen to be absorbed (or desorbed) from water.

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Rate of oxygen absorption

This must be seen as different from solubility.

Imagine that you and I each need to have $600 every month to pay our mortgage, but suppose I make $4 per hour and you make $40 per hour.

It takes you 15 hours to get your $600.

It takes me 150 hours to get my $600.

That is the difference between the rate of absorption and the solubility.

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Rate of oxgyen absorption

Solubility is 8 mg/L, but if you boil water (decrease the solubility), there is less oxygen in the water. If you then cool it down, it takes some time for the oxygen in the atmosphere to dissolve to the MAX (solubility).

The solution may be unsaturated for a time.

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It's the fish tank

That's why fish tanks have bubblers in them. It is an attempt to increase the rate at which the oxygen dissolves to keep it saturated.

It's also why water treatment facilities have aeration devices.

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The α that goes with the β

There is a corresponding value to represent the rate of oxygen absorption of water systems:

$$\alpha = \frac{\text{actual rate of } O_2 \text{ absorption (mg/L s)}}{\text{theoretical rate (mg/L s)}}$$

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The α that goes with the β

In pure water,

$\alpha = 1$

$\beta = 1$

In "impure" water,

$1 > \alpha > 0.4$ (heavily polluted waters)

$1 > \beta > 0.8$ (heavily polluted waters)

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Oxygen content

It can be expressed simply in terms of α and β, for a given set of conditions.

The Lake Ontario shoreline (20°C, 0.94 atm) was analyzed for oxygen content and it was determined that α=0.89, β=0.93.

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The Double-Edged Sword

If you have a polluted body of water (say a small pond) and no dumping or clean-up is attempted, what happens over time?

Some material will settle out into the sediment.
Some material will be oxidized.
Some materials will be decomposed by bacteria.

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The Double-Edged Sword

Some material will settle out into the sediment. (no oxygen required)
Some material will be oxidized. (oxygen required)
Some materials will be decomposed by bacteria. (oxygen often required)

2 out of 3 natural “cleaning” mechanisms usually require oxygen!

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The Double-Edged Sword

Dirty water has less oxygen than clean water - β
It is slower for dirty water to dissolve oxygen – α

The very waters that need the most oxygen have the least!

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Determining oxygen content

The challenges:

1. Oxygen can be lost to or gained from the air after collection. (usually gained)
2. Titration of the oxygen will force additional oxygen to dissolve.

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Collection of water samples

Special sample collection devices must be used that seal with no air.

The simplest collection device is a glass bottle with an air tight cap.

Bottle needs to be overfilled then capped.

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"Fixing" the oxygen content

Immediately after collection, sometimes before reaching the lab, the oxygen content of the samples is "fixed" by conversion to another material that is later titrated in the lab.

Even after fixing, you need to minimize biological activity in the samples that could create new oxygen by "chewing" on the chemicals.

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How do you minimize biological activity?

Ice – if you aren't warm blooded, you always slow down in the cold.

Dark – many water species are photosynthetic and can't do anything in the dark.

Poison – add enough chemicals in the fixing process to kill a lot of the normal biological species in the water sample.

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Methods of analysis

The Winkler Method

- the most famous method, although perhaps not the most popular anymore.
- usually most accurate for relatively pure waters, prone to errors due to inteference from things like Fe^{2+}, SO_3^{2-}, Fe^{3+}

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The Winkler Fixing

Addition of Mn^{2+} and an alkali-iodide (OH^- and I^- mixture) fixes the oxygen. If there is no oxygen present:

$Mn^{2+} + 2\ OH^- \rightarrow Mn(OH)_{2\ (s)}$

And a white solid is observed.

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The Winkler Fixing – 1st step

If there is oxygen present:

$Mn^{2+} + 2\ OH^- + ½\ O_2 \rightarrow MnO_{2\ (s)} + H_2O$

This reaction can also be written as:
$2\ Mn^{2+} + 4\ OH^- + O_2 \rightarrow 2\ MnO_{2\ (s)} + 2\ H_2O$
or
$Mn(OH)_2 + ½\ O_2 \rightarrow MnO_{2\ (s)} + H_2O$

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The Winkler Fixing – 1st step

$Mn^{2+} + 2\ OH^- + ½\ O_2 \rightarrow MnO_{2\ (s)} + H_2O$

The first step converts the dissolved oxygen to MnO_2 solid.

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The Winkler Fixing – 2nd step

Sulfuric acid is added. This neutralizes the OH^- and allows the MnO_2 to oxidize the iodide:

$MnO_{2\,(s)} + 2\ I^- + 4\ H^+ \rightarrow Mn^{2+} + I_2 + 2\ H_2O$

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The Winkler Fixing

$Mn^{2+} + 2\ OH^- + ½\ O_2 \rightarrow MnO_{2\,(s)} + H_2O$

$MnO_{2\,(s)} + 2\ I^- + 4\ H^+ \rightarrow Mn^{2+} + I_2 + 2\ H_2O$

Do you see the brilliance of this two-step sequence?

The first step converts O_2 to MnO_2 under basic conditions. The second step converts MnO_2 to I_2 under acidic conditions. When you acidify the solution – you prevent the first reaction!!! Any oxygen that dissolves later can't react!

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Analyzing the oxygen content

Once it is "fixed" – converted to I_2 – we can analyze the amount of I_2 present and, therefore, the amount of oxygen originally present.

How would you analyze the I_2 present?

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We've seen it before:

The Residual chlorine determination converted Cl_2 to I_2, then analyzed the I_2 by titration with sodium thosulfate!

$I_2 + 2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ I^-$

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So, there are 3 reactions:

$Mn^{2+} + 2\ OH^- + \frac{1}{2}\ O_2 \rightarrow MnO_{2\ (s)} + H_2O$

$MnO_{2\ (s)} + 2\ I^- + 4\ H^+ \rightarrow Mn^{2+} + I_2 + 2\ H_2O$

$I_2 + 2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ I^-$

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A sample problem:

250.0 mL of waste water is collected and fixed using the Winkler method. Titration of the sample yields a starch-iodide endpoint after addition of 12.72 mL of a standardized 0.0187 M sodium thiosulfate solution. What is the oxygen content of the wastewater expressed in mg/L?

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Where would you start?

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Where would you start?

Moles! Moles! Moles!

12.72 mL $Na_2S_2O_3$ * 0.0187 M $Na_2S_2O_3$ =

0.2379 mmol $Na_2S_2O_3$

And so…

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So, there are 3 reactions:

$Mn^{2+} + 2\ OH^- + ½\ O_2 \rightarrow MnO_{2\ (s)} + H_2O$

$MnO_{2\ (s)} + 2\ I^- + 4\ H^+ \rightarrow Mn^{2+} + I_2 + 2\ H_2O$

$I_2 + 2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ I^-$

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Where would you start?

0.2379 mmol $Na_2S_2O_3$ * $\frac{1 mol\ S_2O_3^{2-}}{1\ mol\ Na_2S_2O_3}$ =

0.2379 mmol $S_2O_3^{2-}$ * $\frac{1\ mol\ I_2}{2\ mol\ S_2O_3^{2-}}$ * $\frac{1\ mol\ MnO_2}{1\ mol\ I_2}$

= 0.1189 mmol MnO_2 * $\frac{½\ mol\ O_2}{1\ mol\ MnO_2}$ =

0.05947 mmol O_2

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Finishing…

$\frac{0.05947\ mmol\ O_2}{250.0\ mL}$ = 2.379×10^{-4} M O_2

= $\frac{2.379 \times 10^{-4}\ moles\ O_2}{1\ L\ waste\ water}$ * $\frac{32.0\ g\ O_2}{1\ mol\ O_2}$ * $\frac{1000\ mg}{1\ g}$ =

= 7.61 mg/L

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What does that answer mean?

7.61 mg/L – so what?

Saturated pure water at room temp is about 8 mg/L.

$\frac{7.61\ mg/L}{8\ mg/L}$ = 0.95 = β