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COD

Not "Cash on Delivery"

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Chemical Oxygen Demand

Same principle as BOD but different execution.

Rather than biologically decompose/oxidize organic waste, we chemically decompose/oxidize organic waste.

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It all begins with...

...a balanced equation!

$$C_n H_a O_b N_c + d Cr_2 O_7^{2-} + (8d+c) H^+ \rightarrow$$
$$n CO_2 + (a+8d-3c)/2 H_2 O + c NH_4^+ + 2 d Cr^{3+}$$

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Ignoring the stoichiometry for the moment

$$C_nH_aO_bN_c + Cr_2O_7^{2-} + H^+ \xrightarrow{\Delta} CO_2 + H_2O + NH_4^+ + Cr^{3+}$$
$$C_nH_aO_bN_c + O_2 \rightarrow CO_2 + H_2O + NH_3$$

You can't help but notice the similarities!

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The differences

$$C_nH_aO_bN_c + Cr_2O_7^{2-} + H^+ \xrightarrow{\Delta} CO_2 + H_2O + NH_4^+ + Cr^{3+}$$
$$C_nH_aO_bN_c + O_2 \rightarrow CO_2 + H_2O + NH_3$$

NH_4^+ instead of NH_3 . Why?

It's in acid. NH_3 is a base. In acid, it gets protonated.

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The differences

$$C_nH_aO_bN_c + Cr_2O_7^{2-} + H^+ \xrightarrow{\Delta} CO_2 + H_2O + NH_4^+ + Cr^{3+}$$
$$C_nH_aO_bN_c + O_2 \rightarrow CO_2 + H_2O + NH_3$$

$Cr_2O_7^{2-}$ and acid with heat instead of bacteria and oxygen in a warm, dark place.

Other than that, they are really the identical process.

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Where's the O in C-D?

$$C_nH_aO_bN_c + Cr_2O_7^{2-} + H^+ \xrightarrow{\Delta} \rightarrow CO_2 + H_2O + NH_4^+ + Cr^{3+}$$

It's in the dichromate ($Cr_2O_7^{2-}$).

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How to test for COD...

How would you test for COD?

You need to monitor either the disappearance of dichromate or the appearance of Cr^{3+}

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Excess dichromate

Dichromate can be reduced inorganically to Cr^{3+} using Fe^{2+}

$$6 Fe^{2+} + Cr_2O_7^{2-} + 14 H^+ \rightarrow 6 Fe^{3+} + 2 Cr^{3+} + 7 H_2O$$

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To Conduct the test:

Take x mL of the waste water sample to be tested. Add an equal amount of $K_2Cr_2O_7$ solution to the sample and a sample of distilled water (the blank).

After digestion, you titrate both the blank and the waste water sample with an $Fe(NH_4)_2(SO_4)_2$ standard solution.

The difference between the 2 titrations is the amount of $Cr_2O_7^{2-}$ used in the digestion.

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Sample COD problem

A 50 mL waste water sample is collected. 10 mL of 0.25 N $K_2Cr_2O_7$ is added to the water sample and to 50 mL of distilled water. Both samples are heated to 50°C for 30 minutes. The samples are allowed to cool for 10 minutes and then titrated with 0.1015 N iron (II) ammonium sulfate. The waste water sample requires 15.36 mL of titrant, while the blank sample requires 23.65 mL to reach a 1,10 phenanthroline endpoint. What is the COD of the waste water sample?

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Let's break it down:

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What's going on?

You add dichromate to distilled water AND to your water sample.

What does dichromate do in distilled water?

NOTHING! There's nothing for it to oxidize.

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Let's break it down:

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What's going on?

The dichromate is being allowed to react. It is oxidizing organic material!!!

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You can't avoid the stoichiometry

$$6 Fe^{2+} + Cr_2O_7^{2-} + 14 H^+ \rightarrow 6 Fe^{3+} + 2 Cr^{3+} + 7 H_2O$$

The titration reaction has 6:1 stoichiometry of the Fe^{2+} titrant to the $Cr_2O_7^{2-}$.
Titrating the solutions with Fe^{2+} is telling us how much dichromate is left over!

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Let's break it down:

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We have different amounts of dichromate in the 2 different samples, does this make sense?

Yes, we reduced some dichromate in the "dirty" sample while the distilled water should have all the dichromate it started with!

The difference between the two samples is the amount of dichromate reduced and, therefore, the amount of organic material oxidized!

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Normality

You can express solution concentrations (like the Fe^{2+}) in "normality" instead of "molarity".

Do we remember what "normality" is?

Normality = $\frac{\text{equivalent moles of solute}}{\text{L solution}}$

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Normality

This is a redox titration – equivalence is about electrons.

$$6 \text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ \rightarrow 6 \text{Fe}^{3+} + 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$$

Each iron atom transfers 1 electron.
Each dichromate molecule involves 6 electrons.

This means that $1 \text{ M Fe}^{2+} = 1 \text{ N Fe}^{2+}$
 $1 \text{ M Cr}_2\text{O}_7^{2-} = 6 \text{ N Cr}_2\text{O}_7^{2-}$

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Just a titration!

The samples are allowed to cool for 10 minutes and then titrated with 0.1015 N iron (II) ammonium sulfate. The waste water sample requires 15.36 mL of titrant, while the blank sample requires 23.65 mL to reach a 1,10 phenanthroline endpoint.

How do we start?

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Balanced equation

$$6 \text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ \rightarrow 6 \text{Fe}^{3+} + 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$$

And then....?

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$$i_2 M_1 V_1 = i_1 M_2 V_2$$
$$i_{\text{Fe}} M_{\text{Cr}} V_{\text{Cr}} = i_{\text{Cr}} M_{\text{Fe}} V_{\text{Fe}}$$
$$6 * M_{\text{Cr}} * 50 \text{ mL} = 1 * 0.1015 \text{ M} * 15.36 \text{ mL}$$
$$M_{\text{Cr}} = 5.20 \times 10^{-3} \text{ M } \text{Cr}_2\text{O}_7^{2-}$$

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Using Normality

$$N_1 V_1 = N_2 V_2$$
$$N_{Cr} V_{Cr} = N_{Fe} V_{Fe}$$
$$N_{Cr} * 50 \text{ mL} = 0.1015 \text{ N} * 15.36 \text{ mL}$$
$$N_{Cr} = 3.12 \times 10^{-2} \text{ N } Cr_2O_7^{2-}$$

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For the reference water:

$$N_1 V_1 = N_2 V_2$$
$$N_{Cr} V_{Cr} = N_{Fe} V_{Fe}$$
$$N_{Cr} * 50 \text{ mL} = 0.1015 \text{ N} * 23.65 \text{ mL}$$
$$N_{Cr} = 4.80 \times 10^{-2} \text{ N } Cr_2O_7^{2-}$$

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What does this mean?

Pure water:
 $N_{Cr} = 4.80 \times 10^{-2} \text{ N } Cr_2O_7^{2-}$

"Dirty" water:
 $N_{Cr} = 3.12 \times 10^{-2} \text{ N } Cr_2O_7^{2-}$

The difference between the two is the amount reduced! Since the volume is the same, you can just subtract:
 $4.80 \times 10^{-2} \text{ N} - 3.12 \times 10^{-2} \text{ N} = 1.68 \times 10^{-2} \text{ N } Cr_2O_7^{2-}$
reduced

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Still no "O" in C-D!

We could express the impurity based strictly on the dichromate used: the more dichromate required, the more organic material that must have been there.

Then there would be no "O" in C-D which would now simply be DD – dichromate demand.

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Equivalent oxygen

Instead of reporting the dichromate used, the dichromate is converted into equivalent amount of oxygen, as if you were again "burning" the organic waste as in the BOD process:

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

(unbalanced)

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It's the oxygen, dummy!

So, we convert Normality of dichromate used into mg/L of oxygen demand!

It is very easy to do.

How would you convert Molarity to g/L?

Use the molar mass!!!

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Molarity to g/L

$$\frac{\text{Moles oxygen} \cdot 32 \text{ g oxygen}}{\text{L oxygen} \quad \text{mole oxygen}}$$

How would you convert Molarity of dichromate to g/L of equivalent oxygen?

Throw in the stoichiometry!

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Molarity dichromate to g O/L

$$\frac{\text{Moles Cr}_2\text{O}_7^{2-} \cdot x \text{ moles O}_2 \cdot 32 \text{ g O}_2}{\text{L Cr}_2\text{O}_7^{2-} \quad y \text{ mol Cr}_2\text{O}_7^{2-} \quad \text{mole O}_2}$$

You'd need to compare the 2 balanced equations to get the overall stoichiometry

But Normality makes your life easier.

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Normality to g/L

How would you convert Normality to g/L?

Include the "equivalent molar mass"!

What the he** is "equivalent molar mass"?

It's the molar mass of 1 reactive unit.

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It's a redox reaction

An equivalent is...

...an electron

How many electrons does O_2 transfer?

How many electrons does $Cr_2O_7^{2-}$ transfer?

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Can't see the electrons!

Balanced equations don't show electrons.

$$C_7H_8O_2N_2 + Cr_2O_7^{2-} + H^+ \rightarrow CO_2 + H_2O + NH_4^+ + Cr^{3+}$$
$$C_7H_8O_2N_2 + O_2 \rightarrow CO_2 + H_2O + NH_3$$

If I want to see the electrons...what do I have to do?

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Look at the half-reactions!

$$4e^- + O_2 \rightarrow 2 O^{2-}$$
$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

Balance it (6-1/2 steps)

$$14 H^+ + 6e^- + Cr_2O_7^{2-} \rightarrow 2 Cr^{3+} + 7 H_2O$$

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It's a redox reaction

So, the "equivalent mass of oxygen" is...
... 8 g/mol $\left[\frac{32 \text{ g O}_2}{\text{mol O}_2} \cdot \frac{1 \text{ mol O}_2}{4 \text{ moles e}^-} \right]$

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Convert Normality O₂ to g O₂/L

$$N_{\text{O}_2} = \frac{\text{equiv moles O}_2}{\text{L solution}} \cdot \frac{8 \text{ g O}_2}{\text{equiv mole O}_2}$$

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Convert Normality Cr₂O₇²⁻ to g O₂/L

1.68x10⁻² N Cr₂O₇²⁻ reduced = 1.68x10⁻² N O₂
Normality is always 1:1 stoichiometry

$$\frac{1.68 \times 10^{-2} \text{ equiv moles O}_2}{\text{L solution}} \cdot \frac{8 \text{ g O}_2}{\text{equiv mole O}_2} \cdot \frac{1000 \text{ mg}}{1 \text{ g}} =$$

= 134 mg O₂/L

This is the COD of the original sample.

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COD errors

The most common COD errors are due to oxidation of inorganic species.

Dichromate is a powerful oxidant – it will oxidize not only almost all organics but many metals and non-metal ions:

$$6 \text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ \rightarrow 6 \text{Fe}^{3+} + 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$$
$$6 \text{Cl}^- + \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ \rightarrow 3 \text{Cl}_2 + 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$$

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COD errors

As a result, contaminated water will tend to test higher than it should based strictly on the organic contamination.

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COD vs. BOD

They purport to measure the same thing – but they will never agree.

Biggest error in BOD?
BOD tends to err on the low side due to humus (“inedible” organic waste).

Biggest error in COD?
COD tends to err on the high side due to oxidation of inorganic species.

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Using COD

COD is again a relative measure: higher COD = dirtier water.

COD can be used with BOD – they are not a replacement for each other.

COD must be viewed in context of all other tests.

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Comparing all of our “oxygen”

Dissolved oxygen (DO) – amount of actual oxygen dissolved in a water sample. Higher number = purer water

BOD₅ – Actual amount of dissolved oxygen metabolised over 5 days. Higher number = dirtier

BOD – Extrapolated amount of theoretical oxygen that would be needed to completely metabolise organic waste. Higher number = dirtier

COD – Actual amount of oxygen required to completely oxidize organic waste CHEMICALLY. Higher number = dirtier.
