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ALKALINITY

Bicarbonate-carbonate

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Alkalinity is…

…the measure of the ability of a water to neutralize an acid.

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Acidity

Most natural waters are buffered as a result of a carbon dioxide(air)-bicarbonate (limestone – $CaCO_3$) buffer system.

What is a buffer?

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Buffer

Mixture of an acid (or base) and its conjugate base (or acid)

Think of chemical equilibrium as a see-saw:
$CO_2 + H_2O \leftrightarrow H_2CO_3$
$H_2CO_3 \leftrightarrow HCO_3^- + H^+$
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$

$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2\,H^+$

You need to put 2 fat kids on the see-saw!

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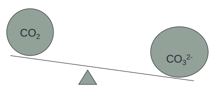
Buffer

$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2\,H^+$



If you have a big heavy weight at both ends of the equilibrium, a small addition of acid or base from an outside source can't change the pH very much.

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Reporting Alkalinity

Alkalinity can be reported in several ways – ways which are not completely chemically accurate.

Alkalinity as $\frac{mg\ CaCO_3\ equivalents}{L}$

$= \frac{\text{ml titrant * Normality of acid * 50,000}}{\text{mL sample}}$

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What's Normality?

Normality is like Molarity with the stoichiometry added right in.

Normality (N) = equivalent moles of solute / L

What's "equivalent" mean? It means you consider the reaction.

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1.5 M HCl

1.5 M HCl

What's HCl?

It's an acid. What's the relevant part of the acid?

H^+

$HCl + OH^- \rightarrow H_2O + Cl^-$

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1.5 M HCl

1.5 M HCl

Since 1 HCl reacts with 1 OH-, there is one chemical equivalent per molecule.

$1.5 \frac{\text{mole HCl}}{\text{L}} * \frac{1\ H^+ \text{ equivalent}}{1\ \text{HCl}} = 1.5\ \text{N HCl}$

$HCl + OH^- \rightarrow H_2O + Cl^-$

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1.5 M H_2SO_4

1.5 M H_2SO_4
What's H_2SO_4?

It's an acid. What's the relevant part of the acid?

H^+

$H_2SO_4 + 2\ OH^- \rightarrow 2\ H_2O + SO_4^{2-}$

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1.5 M H_2SO_4

1.5 M H_2SO_4
Since 1 H_2SO_4 reacts with 2 OH-, there are TWO chemical equivalents per molecule.

$$1.5\ \frac{\text{mole } H_2SO_4}{L} * \frac{2\ H^+ \text{ equivalent}}{1\ H_2SO_4} = 3.0\ N\ H_2SO_4$$

$H_2SO_4 + 2\ OH^- \rightarrow 2\ H_2O + SO_4^{2-}$

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Everyman eats 2 cupcakes

I had 500 cupcakes, I only have 300 left, how many men came through?

$$200\ cupcakes\ eaten \frac{1\ man}{2\ cupcakes} = 100\ men$$

Suppose it was really 50 really hungry women who ate 4 cupcakes each?

If I only care about cupcakes eaten, it doesn't matter:
50 hungry women=100 men

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Metal + polyatomic

$CaCO_3$ (aq) → Ca^{2+} + CO_3^{2-}

The carbonate is the "basic part": it's a negative ion with lots of oxygen, it's going to like H^+

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$

What do you think about HCO_3^-?
ALSO A BASE!
$HCO_3^- + H^+ \rightarrow H_2CO_3$

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Moles! Moles! Moles!

I titrate 50.00 mL of calcium carbonate solution using a 1.5 M H_2SO_4 solution. Equivalence (2nd endpoint) is reached after addition of 32.65 mL of acid. What is the concentration of calcium carbonate in the original sample in mg/L?

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1st thing we need?

Balanced Equation

$CO_3^{2-} + 2 H^+ \rightarrow H_2CO_3$
OR
$CO_3^{2-} + H^+ \rightarrow HCO_3^-$
$HCO_3^- + H^+ \rightarrow H_2CO_3$

You can do it all in one step, or you can do it in two steps. But you aren't done until all the base is gone.

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Moles! Moles! Moles!

$\frac{1.5 \text{ moles } H_2SO_4}{1 \text{ L}} \times 0.03265 \text{ L} = 0.048975 \text{ mol } H_2SO_4$

$0.048975 \text{ mol } H_2SO_4 \times \frac{2 \text{ mol } H^+}{1 \text{ mol } H_2SO_4} = 0.09795 \text{ mol } H^+$

$0.09795 \text{ mol } H^+ \times \frac{1 \text{ mol } CO_3^{2-}}{2 \text{ mol } H^+} = 0.048975 \text{ mol } CO_3^{2-}$

$\frac{0.048975 \text{ mol } CO_3^{2-} \; 1 \text{ mol } CaCO_3}{1 \text{ mol } CO_3^{2-}} = 0.048975 \text{ mol } CaCO_3$

$\frac{0.048975 \text{ mol } CaCO_3}{0.050 \text{ L}} \times \frac{100.09 \text{ g}}{1 \text{ mol } CaCO_3} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 98039 \text{ mg/L}$

98039 mg $CaCO_3$ EQUIVALENTS/L

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Alkalinity as mg/L $CaCO_3$

$= \frac{\text{ml titrant} \times \text{Normality of acid} \times 50{,}000}{\text{mL sample}}$

$= \frac{32.65 \text{ mL} \times 3.0 \text{ N } H_2SO_4 \times 50{,}000}{50 \text{ mL}}$

=97950 mg/L

The expression in the book (or lab) is just the Moles! Moles! Moles! solved for you.

But this is just the TOTAL ALKALINITY.

There are actually different types.

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A base is a base is a base

If you titrate a solution with multiple bases, can you tell what reacts with what?

Essentially, you have 3 different types of bases in the system:

OH- (strong monoprotic base)
CO_3^{2-} (weak diprotic base)
and HCO_3^- (weak monoprotic base)

All 3 can be neutralized by addition of a strong acid.

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Strong vs. Weak

Strong – completely dissociates in water (or other solvent)
Weak – partially dissociates in water

HCl = H+ + Cl^-
100 molecules   100 molecules + 100

$HC_2H_3O_2$ (acetic acid) = H+ + $C_2H_3O_2$-
100 molecules   2   + 2 molecules

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Different pH at endpoints

$H^+ + OH^- \rightarrow H_2O$ (neutral)

$H^+ + CO_3^{2-} \rightarrow HCO_3^-$
(slightly basic)
$HCO_3^- + H^+ \rightarrow H_2CO_3$
(acidic)

$HCO_3^- + H^+ \rightarrow H_2CO_3$
(acidic)

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Different species – Different endpoints

$H^+ + OH^- \rightarrow H_2O$ (neutral – EP1)

$H^+ + CO_3^{2-} \rightarrow HCO_3^-$
(slightly basic – EP1)

$HCO_3^- + H^+ \rightarrow H_2CO_3$
(acidic – EP2)

$HCO_3^- + H^+ \rightarrow H_2CO_3$
(acidic – EP2)

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Different endpoints at different pH values

EP1 – neutral to slightly basic (pH approximately 8)
EP2 – acidic (pH approximately 5)

The key is that everything that happens at EP1 (endpoint #1) happens BEFORE anything happens at EP2.

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Different species – Different endpoints

$H^+ + OH^- \rightarrow H_2O$ (neutral – EP1)

$H^+ + CO_3^{2-} \rightarrow HCO_3^-$
(slightly basic – EP1)

$HCO_3^- + H^+ \rightarrow H_2CO_3$
(acidic – EP2)

$HCO_3^- + H^+ \rightarrow H_2CO_3$
(acidic – EP2)

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IT'S NOT WHAT IT IS…

…IT IS WHAT IT DOES!

Bases accept protons from acids (neutralize acids). That's all they do.

So I refer to the amount of base based on the amount of acid it neutralizes.

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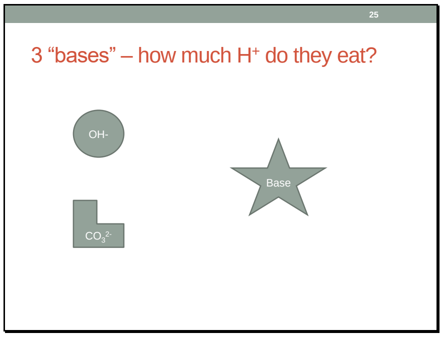

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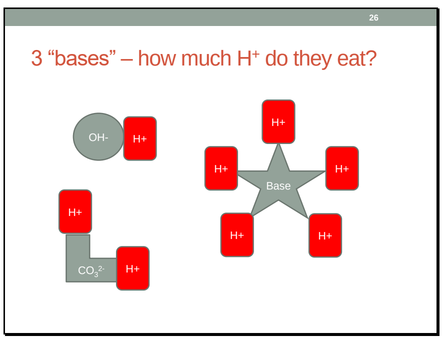

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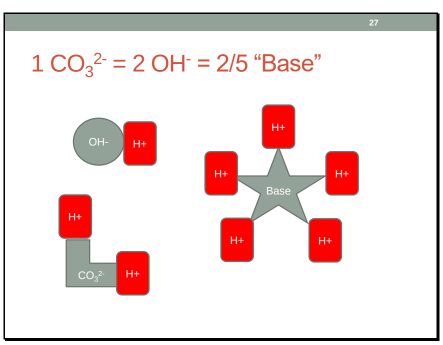

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So if I have 1.25 mol OH^-:

$$1.25\ mol\ OH - \times \frac{1\ mol\ H+}{1\ mol\ OH-} \times \frac{1\ mol\ CO_3 2-}{2\ mol\ H+} = 0.625\ mol\ equiv\ CO_3 2-$$

If I have 1.25 mol "Base"

$$1.25\ mol\ base \times \frac{5\ mol\ H+}{1\ mol\ Base} \times \frac{1\ mol\ CO_3 2-}{2\ mol\ H+} = 3.125\ mol\ equiv\ CO_3 2-$$

It's not about what you really have. It's about how much acid it absorbs relative to carbonate!

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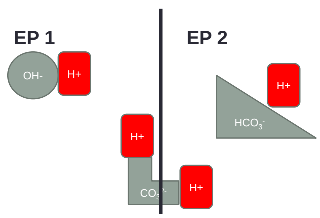
My 3 types of base and their EP



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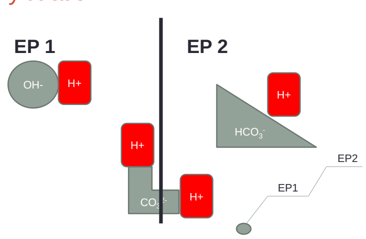
My titration



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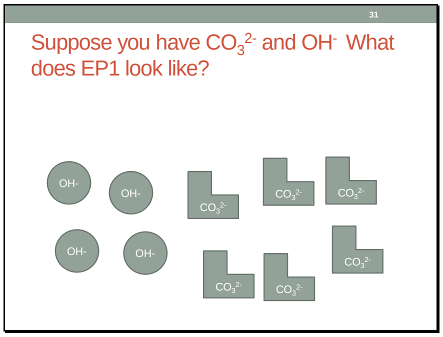

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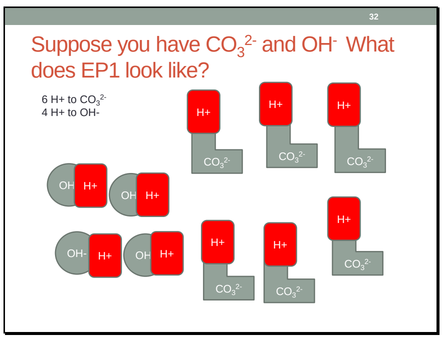

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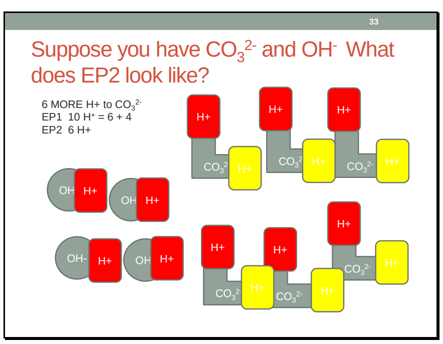

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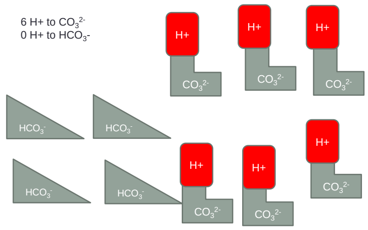
Suppose you have CO_3^{2-} and HCO_3^- EP1?

6 H+ to CO_3^{2-}
0 H+ to HCO_3^-



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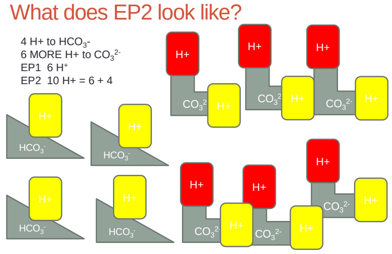
Suppose you have CO_3^{2-} and HCO_3^- What does EP2 look like?

4 H+ to HCO_3^-
6 MORE H+ to CO_3^{2-}
EP1 6 H^+
EP2 10 H+ = 6 + 4



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Example

I titrate a 25.00 mL water sample with 0.1250 M HCl. I achieve the first endpoint at 22.5 mL of HCl and the second after addition of another 27.6 mL of HCl.

What can I conclude?

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Possible	EP1 vol	EP2 vol	Compare
CO_3^{2-}	X	X	EP1 = EP2
HCO_3^-	0	Y	EP1 = 0
OH-	z	0	EP2 =0
CO_3^{2-} HCO_3^-	x	(x+y)	EP1<EP2 EP1 not 0
CO_3^{2-} OH-	(x+z)	X	EP1>EP2 EP2 not 0
HCO_3^- OH-	???	????	????

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OH- is a strong base.

HCO_3^- is a weak acid

If I have more OH- than HCO_3^-, it completely neutralizes it and I just have OH-

If I have more HCO_3^- than OH-, then it partially neutralizes it and I detect only HCO_3^-

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Example

I titrate a 25.00 mL water sample with 0.1250 M HCl. I achieve the first endpoint at 22.5 mL of HCl and the second after addition of another 27.6 mL of HCl.

What can I conclude?

Carbonate and bicarbonate are both present.

How much?

0.1250 M HCl * 0.0225 L HCl = 2.813×10^{-3} mol HCl

2.813×10^{-3} moles CO_3^{2-}

0.1250 M HCl * (0.0276 – 0.0225 L HCl) = 6.375×10^{-4} H+

6.375×10^{-4} moles HCO_3^-

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Units! Units! Units!

Carbonate and bicarbonate are usually measured as "mg equivalent $CaCO_3$/L"
So…

$$0.0225\ L\ HCl \frac{0.1250\ mol\ HCl}{L} = 2.813 \times 10^{-3} mol\ HCl \frac{1\ mol\ H^+}{1\ mol\ HCl} = 2.813 \times 10^{-3} mol\ H^+$$

$$2.813 \times 10^{-3} mol\ H^+ \frac{1\ mol\ CO_3^{2-}}{1\ mol\ H^+} = 2.813 \times 10^{-3} mol\ CO_3^{2-} \frac{1\ mol\ CaCO_3}{1\ mol\ CO_3^{2-}} = 2.813 \times 10^{-3} mol\ CaCO_3$$

$$2.813 \times 10^{-3} mol\ \ CaCO_3 \frac{100.08\ g}{mol\ CaCO_3} \frac{1000\ mg}{g} = 281.5\ mg\ CaCO_3$$

$$\frac{281.5\ mg\ CaCO_3}{0.025\ L} = 11{,}259 \frac{mg\ CaCO_3\ equivalents}{L}$$

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What about the HCO_3^-?

$CO_3^{2-} + 2\ H^+ = H_2CO_3$
$HCO_3^- + H^+ = H_2CO_3$

$$(0.0276\ L\ - 0.0225\ L\ HCl) \frac{0.1250\ mol\ HCl}{L} = 6.375 \times 10^{-4} mol\ HCl \frac{1\ mol\ H^+}{1\ mol\ HCl} = 6.375 \times 10^{-4} mol\ H^+$$

$$6.375 \times 10^{-4} mol\ H^+ \frac{1\ mol\ CO_3^{2-}}{2\ mol\ H^+} = 3.188 \times 10^{-4} mol\ CO_3^{2-} \frac{1\ mol\ CaCO_3}{1\ mol\ CO_3^{2-}} = 3.188 \times 10^{-4} mol\ CaCO_3$$

$$3.188 \times 10^{-4} mol\ \ CaCO_3 \frac{100.08\ g}{mol\ CaCO_3} \frac{1000\ mg}{g} = 31.90\ mg\ CaCO_3$$

$$\frac{31.90\ mg\ CaCO_3}{0.025\ L} = 1276 \frac{mg\ CaCO_3\ equivalents}{L}$$

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Total Alkalinity.

I titrate a 25.00 mL water sample with 0.1250 M HCl. I achieve the first endpoint at 22.5 mL of HCl and the second after addition of another 27.6 mL of HCl. What is the total alkalinity?

Assume the second endpoint is reached and it was all $CaCO_3$ in the sample.

22.5 mL + 27.6 mL = 50.1 mL total HCl

$$(0.0501\ L\ HCl) \frac{0.1250\ mol\ HCl}{L} = 6.2625 \times 10^{-3} mol\ HCl \frac{1\ mol\ H^+}{1\ mol\ HCl} = 6.2625 \times 10^{-3} mol\ H^+$$

$$6.2625 \times 10^{-3} mol\ H^+ \frac{1\ mol\ CO_3^{2-}}{2\ mol\ H^+} \frac{1\ mol\ CaCO_3}{1\ mol\ CO_3^{2-}} = 3.131 \times 10^{-3} mol\ CaCO_3$$

$$3.131 \times 10^{-3} mol\ \ CaCO_3 \frac{100.08\ g}{mol\ CaCO_3} \frac{1000\ mg}{g} = 313.380\ mg\ CaCO_3$$

$$\frac{313.38\ mg\ CaCO_3}{0.025\ L} = 12{,}535\ \frac{mg\ CaCO_3\ equivalents}{L}$$

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Notice…

Total alkalinity = 12,535 mg $CaCO_3$/L

Carbonate alkalinity = 11, 260 mg $CaCO_3$/L

Bicarbonate alkalinity = 1276 mg $CaCO_3$/L

11,260 + 1276 = 12536 mg $CaCO_3$/L!!!!

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Example

I titrate a water sample with 0.1250 M HCl. I achieve the first endpoint at 22.5 mL of HCl and the second after addition of another 27.6 mL of HCl.

What can I conclude?

Carbonate and bicarbonate are both present.

Is this really true?

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Example

I titrate a water sample with 0.1250 M HCl. I achieve the first endpoint at 22.5 mL of HCl and the second after addition of another 27.6 mL of HCl.

Carbonate and bicarbonate are both present.

Is this really true?

No – any chemical species that behaves like carbonate or like bicarbonate will look identical!!!!!!!

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To be totally accurate, I should quote the levels as:

"Bicarbonate and chemical equivalents"

"Carbonate and chemical equivalents"

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Example

I titrate a 50.00 mL water sample with 0.1250 M HCl. I achieve the first endpoint at 22.5 mL of HCl and the second after addition of another 19.6 mL of HCl. What is the total alkalinity in mg $CaCO_3$/L?

What can I conclude about the species present?

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Possible	EP1 vol	EP2 vol	Compare
CO_3^{2-}	X	X	EP1 = EP2
HCO_3^-	0	Y	EP1 = 0
OH-	z	0	EP2 =0
CO_3^{2-} HCO_3^-	x	(x+y)	EP1<EP2 EP1 not 0
CO_3^{2-} OH-	(x+z)	X	EP1>EP2 EP2 not 0
HCO_3^- OH-	???	????	????

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Example

I titrate a 50.00 mL water sample with 0.1250 M HCl. I achieve the first endpoint at 22.5 mL of HCl and the second after addition of another 19.6 mL of HCl. What is the total alkalinity in mg $CaCO_3$/L?

What can I conclude?

Carbonate and OH- are both present.

BUT if I only care about total alkalinity I just ASSUME it is all $CaCO_3$!!!!

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Total alkalinity:

22.5 mL + 19.6 mL = 42.1 mL

$$(0.0421\ L\ HCl)\frac{0.1250\ mol\ HCl}{L} = 5.2625 \times 10^{-3} mol\ HCl \frac{1\ mol\ H^+}{1\ mol\ HCl} = 5.2625 \times 10^{-3} mol\ H^+$$

$$5.2625 \times 10^{-3} mol\ H^+ \frac{1\ mol\ CO_3^{2-}}{2\ mol\ H^+}\frac{1\ mol\ CaCO_3}{1\ mol\ CO_3^{2-}} = 2.631 \times 10^{-3} mol\ CaCO_3$$

$$2.631 \times 10^{-3} mol\ \ CaCO_3 \frac{100.08\ g}{mol\ CaCO_3}\frac{1000\ mg}{g} = 263.34\ mg\ CaCO_3$$

$$\frac{263.34\ mg\ CaCO_3}{0.050\ L} = 5267\ \frac{mg\ CaCO_3\ equivalents}{L}$$

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Hydroxide alkalinity

22.5 mL EP1 – 19.6 mL EP2 = 2.9 mL excess

0.1250 M HCl (0.0029 L) = moles H^+ $\frac{1\ mol\ CaCO_3}{2\ mol\ H^+}$ = mol $CaCO_3$