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Question 1 (7 points)

You titrate 10.00 mL of 0.100 M NH_4Cl with 0.100 M NaOH. Calculate the pH after each 1.00 mL addition of NaOH from 0.00 mL to 12.00 mL of NaOH added.

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0.00 mL

$NH_4^+ + H_2O = NH_3 + H_3O^+$ $K_a = \frac{K_w}{K_b} = \frac{1.0\text{x}10^{-14}}{1.8\text{x}10^{-5}}$

I	0.100 M	-	0	0
C	-x	-	+x	+x
E	0.100-x	-	x	x

x=7.45x10^{-6} $5.56x10^{-10} = \frac{x * x}{0.100 - x}$

pH = -log (7.45x10^{-6}) = 5.12

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1.00 mL – moles is better

$NH_4^+ + OH^- = NH_3 + H_2O$

0.001 mol	0.0001 mol		0	0
-0.0001 mol	-0.0001 mol		+0.0001 mol	
0.0009 mol	0		0.00001 mol	

It’s a BUFFER!!!

$NH_4^+ + H_2O = NH_3 + H_3O^+$

pH = pK_a + log [base]/[acid]

pH = -log (5.56×10^{-10}) + log (0.0001/0.0009)

pH = 9.25 + (-0.95)=8.3

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2.00 mL – moles is better

$NH_4^+ + OH^- = NH_3 + H_2O$

0.0009 mol	0.0001 mol		0.0001	0
-0.0001 mol	-0.0001 mol		+0.0001 mol	
0.0008 mol	0		0.0002 mol	

It’s a BUFFER!!!

$NH_4^+ + H_2O = NH_3 + H_3O^+$

pH = pK_a + log [base]/[acid]

pH = 9.25 + log (0.0002/0.0008)

pH = 9.25 + (-0.60)=8.65

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3, 4, 5 mL etc

pH = 9.25 + log (0.0003/0.0007) = 8.88

pH = 9.25 + log (0.0004/0.0006) = 9.07

pH = 9.25 + log (0.0005/0.0005) = 9.25

pH at ½ equivalence = pKa

pH = 9.25 + log (0.0006/0.0004) = 9.42

pH = 9.25 + log (0.0007/0.0003) = 9.62

pH = 9.25 + log (0.0008/0.0002) = 9.85

pH = 9.25 + log (0.0009/0.0001) = 10.20

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At equivalence = It's all NH_3

It's just a K_b problem of NH_3!!!
0.100 M * 10/20 = 0.05 M NH_3
$NH_3 + H_2O = NH_4^+ + OH^-$
0.05 M - 0 0
-x - +x +x
0.05-x x x
$1.8x10^{-5} = X^2/0.05-x$
$X=9.48x10^{-4}$
pOH = -log ($9.48x10^{-4}$ = 3.02
pH = 14-3.02 = 10.98

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11 mL

11 mL is just like adding 1 mL

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Question #2 (8 points)

You have 500 mL of a solution that is 0.100 M in each of Ni^{2+} ions, Ca^{2+} ions, and Pb^{2+} ions. You wish to selectively precipitate the metal ions by adding Na_2CO_3 (s). What is the first ion to precipitate? How much (g) Na_2CO_3 do you need to add to start to precipitate the first ion? What is the second ion to precipitate? How much TOTAL Na_2CO_3 do you need to add to start to precipitate the second ion? How much TOTAL Na_2CO_3 do you need to add to start to precipitate the third ion? How much TOTAL Na_2CO_3 do you need to add to precipitate all three ions?

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Solubility – check the K_{sp}

$K_{sp}(PbCO_3) = 7.4 \times 10^{-14}$
$K_{sp}(CaCO_3) = 3.3 \times 10^{-9}$
$K_{sp}(NiCO_3) = 1.3 \times 10^{-7}$

The smallest K_{sp} is least soluble so it goes first. So: Pb^{2+} precipitates first, followed by Ca^{2+} and then Ni^{2+}
Note: this is only because the concentrations are identical, you need to consider the K-equation in total.

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1st ion

$K_{sp}(PbCO_3) = 7.4 \times 10^{-14} = [Pb^{2+}][CO_3^{2-}]$

$7.4 \times 10^{-14} = [0.100\ M][CO_3^{2-}]$
$[CO_3^{2-}] = 7.4 \times 10^{-13}\ M$

In other words, as soon as the concentration of carbonate reaches 7.4×10^{-13} M, your solution is saturated with $PbCO_3$ and any more carbonate starts it precipitating.

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$$7.4 \times 10^{-13} M\ CO_3^{2-} \times \frac{1\ mol\ Na_2CO_3}{1\ mol\ CO_3^{2}} = 7.4 \times 10^{-13} M\ Na_2CO_3$$

$$7.4 \times 10^{-13} \frac{mol\ Na_2CO_3}{L} \times 0.500\ L = 3.7 \times 10^{-13} mol\ Na_2CO_3$$

$$3.7 \times 10^{-13}\ mol\ Na_2CO3 \times \frac{106.01\ g}{mol\ Na_2CO_3} = 3.92 \times 10^{-11} g$$

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2nd ion

$K_{sp}(CaCO_3) = 3.3x10^{-9} = [Ca^{2+}][CO_3^{2-}]$

$3.3x10^{-9} = [0.100 M][CO_3^{2-}]$
$[CO_3^{2-}] = 3.3x10^{-8}$ M

In other words, as soon as the concentration of carbonate reaches $3.3x10^{-8}$ M, your solution is saturated with $CaCO_3$ and any more carbonate starts it precipitating. BUT TO GET THERE, YOU MUST 1ST PRECIPITATE THE LEAD!

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When the Pb is precipitating, the concentration of CO_3^{2-} isn't going up very quickly because the $PbCO_3$ is precipitating.

You can calculate how much Pb is left.

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How much Pb precipitates?

$K_{sp}(PbCO_3) = 7.4x10^{-14} = [Pb^{2+}][CO_3^{2-}]$

$7.4x10^{-14} = [x][3.3x10^{-8} M]$
$[Pb^{2+}] = 2.24x10^{-6}$ M

In other words, almost all (99.998%) of the original 0.100 M Pb^{2+} has to precipitate before the Ca^{2+} can start.

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Amount added to ppt all Pb

0.100 M Pb x 0.500 L = 0.05 mol Pb

0.05 mol Pb x (1 mol Na_2CO_3/1 mol Pb) = 0.05 mol Na_2CO_3

0.05 mol Na_2CO_3 x (106.01 g/mol) = 5.30 g added

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For the $CaCO_3$ in solution

$$3.3 \times 10^{-8}\ M\ CO_3^{2-} \times \frac{1\ mol\ Na_2CO_3}{1\ mol\ CO_3^{2}} = 3.3 \times 10^{-8} M\ Na_2CO_3$$

$$3.3 \times 10^{-8} \frac{mol\ Na_2CO_3}{L} \times 0.500\ L = 1.65 \times 10^{-8} mol\ Na_2CO_3$$

$$1.65 \times 10^{-8}\ mol\ Na_2CO3 \times \frac{106.01\ g}{mol\ Na_2CO_3} = 1.75 \times 10^{-6} g$$

The amount of Na_2CO_3 dissolved is insignificant. It takes a total of 5.30 g of Na_2CO_3 to get the lead out! (and start the Ca precipitating)

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3rd ion

$K_{sp}(NiCO_3) = 1.3x10^{-7} = [Ni^{2+}][CO_3^{2-}]$

$1.3x10^{-7} = [0.100\ M][CO_3^{2-}]$
$[CO_3^{2-}] = 1.3x10^{-6}$ M

As soon as the concentration of carbonate reaches $1.3x10^{-6}$ M, your solution is saturated and it starts precipitating. BUT, to get there you must first precipitate the Pb AND most of the Ca!!!

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How much Ca precipitates?

$K_{sp}(CaCO_3) = 3.3x10^{-9} = [Ca^{2+}][CO_3^{2-}]$

$3.3x10^{-9} = [x][1.3x10^{-6} M]$

$[Ca^{2+}] = 2.54x10^{-3} M$

In other words, almost all (97.5%) of the original 0.100 M Pb^{2+} has to precipitate before the Ca^{2+} can start.

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0.100 M original Ca – $2.54x10^{-3}$ M left = $9.75x10^{-2}$ M precipitated

$9.75x10^{-2}$ mol/L * 0.500 L = $4.875x10^{-2}$ mol Ca^{2+}

$4.875x10^{-2}$ mol Ca^{2+} * (1 mol Na_2CO_3/1mol Ca^{2+}) = $4.875x10^{-2}$ mol Na_2CO_3

$4.875x10^{-2}$ mol Na_2CO_3 (106.01 g/mol) = 5.17 g

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Amount in solution?

$1.3x10^{-6}$ M CO_3^{2-} * 0.500 L = $6.5x10^{-7}$ mol CO_3^{2-}

$6.5x10^{-7}$ mol Na_2CO_3 * (106.01 g/mol) = $6.89x10^{-5}$ g in solution

Again, the amount in solution is insignificant relative to the amount precipitated.

The TOTAL amount added to start the 3rd precipitation = 5.30 g + 5.17 g = 10.47 g

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You can see where this is going…

The total amount precipitated when all 3 are "done" is:

0.100 M + 0.100 M + 0.100 M = 0.300 M total ions

0.300 mol/L * 0.5 L = 0.150 mol ions
0.150 mol ions * (1 Na_2CO_3/1mol ions) * (106.01 g/mol) = 15.90 g ions.

What about the sodium carbonate IN SOLUTION?

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When is it all gone?

We start with 0.100 M Ni^{2+} when is "gone"? Let's say when 0.0001 M is left (only had 3 sig figs to begin with)

$K_{sp}(NiCO_3) = 1.3x10^{-7} = [Ni^{2+}][CO_3^{2-}]$

$1.3x10^{-7} = [0.0001\ M][CO_3^{2-}]$
$[CO_3^{2-}] = 1.3x10^{-3}$ M

Now there is some in solution worth mentioning:

$1.3x10^{-3}$ M * 0.5 L = $6.5x10^{-4}$ mol * (106.01 g/mol) = $6.9x10^{-2}$ g

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TOTAL total

15.90 g precipitated + 0.07 g still in solution = 15.97 g total Na_2CO_3 added