

Chemistry 301 - PROBLEM SET #2 - ANSWERS

- 1) For a solution having 1.00×10^{-3} equivalents/litre carbonate alkalinity, and a $[H^+]$ of 4.69×10^{-10} , what is the percentage contribution to alkalinity from CO_3^{2-} ?

Remember that: Carbonate alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$

To calculate the percentage contribution from CO_3^{2-} , we need to know $[CO_3^{2-}]$ as well as the total Carbonate alkalinity, which is given as 1.00×10^{-3} equivalents/litre.

From the given $[H^+]$ of 4.69×10^{-10} M, we can calculate pH and $([OH^-] - [H^+])$

$$pH = -\log [H^+] = 9.33$$

$$[OH^-] - [H^+] \cong [OH^-] = (1.00 \times 10^{-14}) / (4.69 \times 10^{-10}) = 2.13 \times 10^{-5}$$

(can ignore $[H^+]$ at this pH >7.0)

From the pH or $[H^+]$, along with K_{a2} , we can calculate $[CO_3^{2-}] / [HCO_3^-]$:

$$K_{a2} = [CO_3^{2-}][H^+] / [HCO_3^-]; \quad pK_{a2} = 10.33$$

$$pK_{a2} = pH - \log [CO_3^{2-}] / [HCO_3^-]$$

$$\log [CO_3^{2-}] / [HCO_3^-] = pH - pK_{a2} = 9.33 - 10.33 = -1.00$$

$$[CO_3^{2-}] / [HCO_3^-] = 0.10$$

$$[CO_3^{2-}] = 0.10[HCO_3^-], \text{ or } [HCO_3^-] = 10[CO_3^{2-}]$$

Substitute into Carb. Alk. = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] = 1.00 \times 10^{-3}$ eq/l

$$10[CO_3^{2-}] + 2[CO_3^{2-}] + (2.13 \times 10^{-5}) = 1.00 \times 10^{-3}$$

$$12[CO_3^{2-}] = (1.00 \times 10^{-3}) - (2.13 \times 10^{-5}) = 9.79 \times 10^{-4}$$

$$[CO_3^{2-}] = \mathbf{8.16 \times 10^{-5}}$$

Finally, what is percentage contribution to alkalinity from CO_3^{2-} ?

$$\text{percentage contribution} = (2[CO_3^{2-}] / \text{total Carb. Alk.}) \times 100$$

(2 x since carbonate contributes doubly, being able to absorb 2 protons,
and x 100 since we want percent contribution rather than fractional)

$$= 2(8.16 \times 10^{-5}) / (1.00 \times 10^{-3}) \times 100 = \mathbf{16.3\%}$$

2) A water sample is taken from the bottom of a lake in an area containing a lot of limestone - $\text{CaCO}_3(\text{s})$. This sample is measured to have a pH of 7.5 and a dissolved Ca concentration ($[\text{Ca}^{2+}]$) of 150 ppm. (Note: atmospheric CO_2 not given, as you do not need to assume equilibrium with the atmosphere for this problem).

a. Calculate the expected concentrations of CO_3^{2-} and HCO_3^- if equilibrium with $\text{CaCO}_3(\text{s})$ is assumed. (report your answer in M [moles/L] with 2 significant figures)

$$\text{Given dissolved } \text{Ca}^{2+} = [\text{Ca}^{2+}] = 150 \text{ ppm} = 150 \text{ mg/L} = \frac{(0.150 \text{ g/L})}{(40.08 \text{ g/mol})} = 3.74 \times 10^{-3} \text{ M}$$

For $[\text{CO}_3^{2-}]$ determination, look at equilibrium with limestone, $\text{CaCO}_3(\text{s})$:

$$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} \quad K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 4.47 \times 10^{-9} \quad (\text{from lecture notes})$$

$$[\text{CO}_3^{2-}] = \frac{K_{\text{sp}}}{[\text{Ca}^{2+}]} = \frac{(4.47 \times 10^{-9})}{(3.74 \times 10^{-3})} = \mathbf{1.19 \times 10^{-6} \text{ M}}$$

$$\text{For } [\text{HCO}_3^-], \text{ use } K_{\text{a}2} \text{ equilibrium, } K_{\text{a}2} = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}$$

$$(\text{p}K_{\text{a}2} = 10.33 \therefore K_{\text{a}2} = 10^{-10.33} = 4.67 \times 10^{-11})$$

$$(\text{pH} = 7.50 \therefore [\text{H}^+] = 10^{-7.5} = 3.16 \times 10^{-8})$$

$$[\text{HCO}_3^-] = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{K_{\text{a}2}} = \frac{(1.19 \times 10^{-6})(3.16 \times 10^{-8})}{(4.67 \times 10^{-11})} = \mathbf{8.05 \times 10^{-4} \text{ M}}$$

b. What is the total carbonate alkalinity of the water?

$$\text{At pH} > 7 \therefore \text{Carbonate alkalinity} \cong [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (\text{can ignore } \text{H}^+)$$

know $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ from part a., calculate $[\text{OH}^-]$ from pH:

$$[\text{OH}^-] = K_{\text{w}} / [\text{H}^+] = (1.00 \times 10^{-14}) / (3.16 \times 10^{-8}) = 3.16 \times 10^{-7}$$

$$(\text{or, } \text{pOH} = 14 - \text{pH} = 14 - 7.5 = 6.5, [\text{OH}^-] = 10^{-6.5} = 3.16 \times 10^{-7})$$

$$\text{Carbonate alkalinity} = (8.05 \times 10^{-4}) + 2(1.19 \times 10^{-6}) + (3.16 \times 10^{-7}) = 8.08 \times 10^{-4} \text{ eq/L}$$

$$\mathbf{\text{Carbonate alkalinity} = 0.81 \text{ meq/L}}$$

3) Water hardness is sometimes removed by the addition of lime ($\text{Ca}(\text{OH})_2$):



If the concentration of Ca^{2+} in a lake is $5.00 \times 10^{-3} \text{ M}$, what mass of lime will be needed to soften 1 litre of this lake water (in g)?

For each mole of Ca^{2+} in the water, we must add 1 mole of $\text{Ca}(\text{OH})_2(\text{s})$. Since we are given $[\text{Ca}^{2+}]$, we can calculate the amount of $\text{Ca}(\text{OH})_2(\text{s})$ needed. One litre of water contains 5.00×10^{-3} moles of Ca^{2+} , need 5.00×10^{-3} moles of $\text{Ca}(\text{OH})_2(\text{s})$ (MW = 74.1)

$$\mathbf{\text{Mass of lime needed per litre} = (5.00 \times 10^{-3} \text{ mole}) (74.1 \text{ g/mole}) = 0.371 \text{ g } \text{Ca}(\text{OH})_2(\text{s})}$$

4) Given a total lead concentration of $2.0 \times 10^{-5} \text{ M}$, a total NTA concentration of $2.0 \times 10^{-2} \text{ M}$, and a pH of 12.3 (note extreme pH)

a. Under these conditions, what is the dominant form of NTA?

Relevant equation is: $\text{H(NTA)}^{-2} \rightleftharpoons \text{H}^{+} + (\text{NTA})^{-3}$ $\text{pK}_{\text{a}3} = 10.28$
 Since the pH is higher than $\text{pK}_{\text{a}3}$, the product will dominate - **(NTA)⁻³ is dominant form**
 (since it is ~2 units higher than $\text{pK}_{\text{a}3}$, the ratio of $(\text{NTA})^{-3}$ to H(NTA)^{-2} will be ~100:1)

b. What is the ratio of $[\text{Pb}^{2+}]$ to $[\text{Pb(NTA)}^{-}]$?

Relevant equation is: $\text{Pb}^{2+} + (\text{NTA})^{-3} \rightleftharpoons \text{Pb(NTA)}^{-}$ $\text{pK}_{\text{f}} = -11.4$

$$K_{\text{f}} = \frac{[\text{Pb(NTA)}^{-}]}{[\text{Pb}^{2+}][(\text{NTA})^{-3}]} = 2.5 \times 10^{11} \quad \text{or} \quad \frac{[\text{Pb}^{2+}]}{[\text{Pb(NTA)}^{-}]} = \frac{1}{K_{\text{f}}[(\text{NTA})^{-3}]}$$

assume that $[(\text{NTA})^{-3}] = \text{total NTA}$, since total NTA \gg total lead

$$\frac{[\text{Pb}^{2+}]}{[\text{Pb(NTA)}^{-}]} = \frac{1}{(2.5 \times 10^{11})(2.0 \times 10^{-2})} = \mathbf{2.0 \times 10^{-10}}$$

(almost all of the lead is complexed to NTA)

c. What is the predicted $[\text{Pb}^{2+}]$, considering NTA complexation only?

We know: 1) Total lead = $[\text{Pb}^{2+}] + [\text{Pb(NTA)}^{-}] = 2.0 \times 10^{-5} \text{ M}$

$$2) \frac{[\text{Pb}^{2+}]}{[\text{Pb(NTA)}^{-}]} = \frac{1}{(2.5 \times 10^{11})(2.0 \times 10^{-2})} = 2.0 \times 10^{-10}$$

2 equations, 2 unknowns, solve for $[\text{Pb}^{2+}]$. Can simplify first equation, knowing that virtually all of the lead is complexed, so $[\text{Pb(NTA)}^{-}] = 2.0 \times 10^{-5} \text{ M}$. Plug in to equation 2):

$$[\text{Pb}^{2+}] = (2.0 \times 10^{-5})(2.0 \times 10^{-10}) = \mathbf{4.0 \times 10^{-15} \text{ M}}$$

d. Does this concentration of $[\text{Pb}^{2+}]$ exceed the solubility of $\text{Pb(OH)}_2(\text{s})$ under these conditions? If so, what do you think will happen?

Relevant equation is: $\text{Pb(OH)}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+} + 2\text{OH}^{-}$ $\text{pK}_{\text{sp}} = 19.79$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{OH}^{-}]^2 = 10^{-19.79} = 1.62 \times 10^{-20}$$

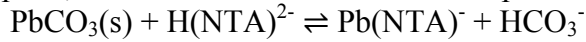
At pH = 12.3, $[\text{H}^{+}] = 5.01 \times 10^{-13} \text{ M}$, $[\text{OH}^{-}] = 10^{-14}/[\text{H}^{+}] = 0.02 \text{ M}$

$$[\text{Pb}^{2+}] \text{ at saturation} = K_{\text{sp}}/[\text{OH}^{-}]^2 = (1.62 \times 10^{-20})/(0.02)^2 = \mathbf{4.0 \times 10^{-17} \text{ M}}$$

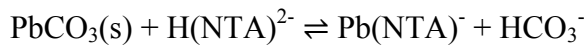
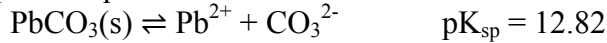
Since the observed $[\text{Pb}^{2+}]$ is greater than the saturation concentration, the solution is supersaturated with respect to $\text{Pb(OH)}_2(\text{s})$. This is true even at these low levels, due to the high pH. We therefore expect some $\text{Pb(OH)}_2(\text{s})$ to precipitate out.

- 5) After a low concentration of NTA has equilibrated with $\text{PbCO}_3(\text{s})$ at pH 7.00 in a medium having a final HCO_3^- concentration of $7.50 \times 10^{-4} \text{M}$, what is the ratio of $[\text{Pb}(\text{NTA})^-]$ to $[\text{H}(\text{NTA})^{2-}]$ in this solution?

At pH 7, both carbonate and NTA will be protonated, relevant reaction is:



Separate equations:



$$K_{\text{T}} = \frac{[\text{Pb}(\text{NTA})^-][\text{HCO}_3^-]}{[\text{H}(\text{NTA})^{2-}]}, \quad \text{p}K_{\text{T}} = \text{p}K_{\text{sp}} + \text{p}K_3 + \text{p}K_{\text{f}} - \text{p}K_2 = 1.37,$$

$$K_{\text{T}} = 4.27 \times 10^{-2}$$

(note that, due to round off error, we get a slightly different value than we got in class using K 's, rather than these $\text{p}K$'s given in your table)

Now, if $[\text{HCO}_3^-] = 7.50 \times 10^{-4} \text{M}$ and $\text{pH} = 7.00$,

$$\frac{[\text{Pb}(\text{NTA})^-]}{[\text{H}(\text{NTA})^{2-}]} = \frac{K_{\text{T}}}{[\text{HCO}_3^-]} = \frac{(4.27 \times 10^{-2})}{(7.50 \times 10^{-4})} = 57 \quad (\text{would be } 55 \text{ with } K_{\text{T}} = 4.1 \times 10^{-2})$$

(both answers will be counted as correct – whether you use the $\text{p}K$'s in the table or the constants in the lecture notes)