Name  *Key*

CH 222     Quantitative Analysis     Test 3     April 10, 2014

Be sure to show units in your numerical work.  You must express answers with the correct number of digits!

1.     The $K_{sp}$ of $CaCO_3$ is (4.5)×$10^{-9}$  *(2 digit)*.  The concentration of Ca in sea water is 0.0(103) M  *(3 digits)*.
Compute $pCO_3$ in sea water if sea water is a saturated solution of calcium carbonate.

$$K_{sp} = [Ca^{+2}][CO_3^{-2}]$$

$$[CO_3^{-2}] = \frac{K_{sp}}{[Ca^{+2}]} \quad \underline{\text{Take } -\log_{10}}$$

$$pCO_3 = pK_{sp} - pCa$$
$$= 8.35 - 1.987 = \underline{6.36} \quad \text{two digits}$$

2.     The Ksp of AgBr is (5.0)×$10^{-13}$  *(2 digits)*.  Suppose you titrate a solution of NaBr with $AgNO_3$.
What is the concentration of $Ag^+$ at the equivalence point?

$$K_{sp} = [Ag^+][Br^-]$$

at eq pt  $[Ag^+] = [Br^-] = x$

$$x^2 = K_{sp} \Rightarrow x = \sqrt{K_{sp}} = \underline{7.1 \times 10^{-7} \, M}$$
$$\text{two digits}$$

3.     What is the general chemical behavior of EDTA?  Is it best characterized by Bronsted-Lowry or Lewis acid-base theory?  Your answer must include an example!

EDTA is a chelating agent, a multidentate ligand that engulfs metal ions. As it does this, it donates lone pairs of electrons to the metal ion, so it can be viewed as a Lewis base (e⁻ pair donor) and the metal ion can be viewed as a Lewis acid (e⁻ pair acceptor). It does not fit the Bronsted-Lowry definition of an acid-base reaction.

4.a    The fully protonated form of EDTA is called $H_6Y^{+2}$.  Draw its structure.
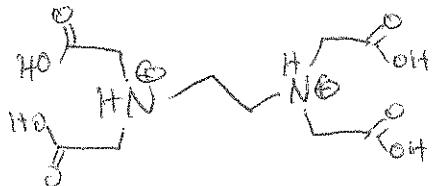


b    When EDTA has two ionizable protons left, it is called $H_2Y^{-2}$.  Draw its structure.
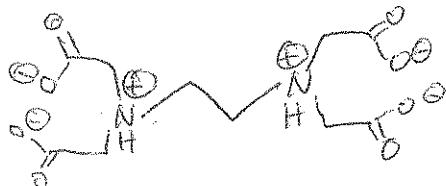


c.    The fully DE-pronated form of EDTA is called $Y^{-4}$.  Draw its structure.
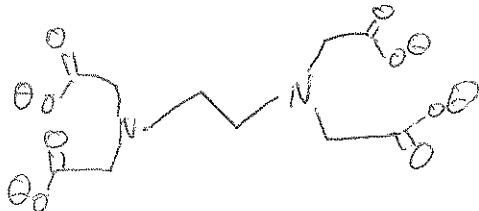


5.    What is [EDTA]?  Which is bigger, [EDTA] or $[Y^{-4}]$?  What is the significance of the quantity $[Y^{-4}]/[EDTA]$?

$[EDTA] = \Sigma [H_nY]$
all forms of protonated EDTA

$\dfrac{[Y^{-4}]}{[EDTA]} = \alpha_{Y-4}$   the fraction that is fully deprotonated and available as a chelating agent.

So $[EDTA] > [Y^{-4}]$

6.    For $BaY^{-2}$, log $K_f$ is 7.86.  For $VY^{-2}$, log $K_f$ is 12.7.  If you mixed up a solution that was 0.02 M in $Ba^{+2}$, 0.02 M in $V^{+2}$, and 0.02 M in EDTA, what would be the dominate chemical species in solution at equilibrium?  Explain.

$\dfrac{[VY^{-2}]}{[V^{+2}][Y^{-4}]} = K_f = 10^{12.7}$

$\dfrac{[BaY^{-2}]}{[Ba^{+2}][Y^{-4}]} = K_f = 10^{7.86}$

$K_f$ for $VY^{-2}$ is greater, so it forms at the expense of $BaY^{-2}$.

Solution will contain $0.02\,M\ Ba^{+2}$ and $0.02\,M\ VY^{-2}$.

7.    For EDTA, $\alpha_{Y-4}$ is $3.7\times10^{-7}$ at pH 5 and $5.4\times10^{-2}$ at pH 9.  Which pH would be more suitable for an EDTA titration of $Ba^{+2}$?  Why?

$K_f' = \alpha_{y-4} K_f$

at pH = 5, $K_f' = (3.7\times10^{-7})10^{7.86} = 27$

at pH = 9, $K_f' = (0.054)10^{7.86} = 3.9\times10^{6}$ ☆

pH 9 would be much better because of the much larger $K_f'$.

8.	You carry out a **strong acid-weak base titration**: 25.00 mls of 0.09271 M $NH_3$ vs 0.1318 M HCl.  What volume of HCl is required to reach the equivalence point?  What is the pH of the titration solution 1 ml before the equivalence point, at the equivalence point, and 1 ml after the equivalence point?  Draw a small and very rough sketch of the titration curve.  The pKa of ammonium ion is 9.244.

$$HCl + NH_3 \rightarrow NH_4^+ + Cl^- \quad \text{titration reaction}$$

$$ml\ HCl = \frac{ml_{NH_3} \times M_{NH_3}}{M_{HCl}} = \frac{25.00\ ml\ (0.09271\ M)}{0.1318\ M} = 17.59\ ml$$
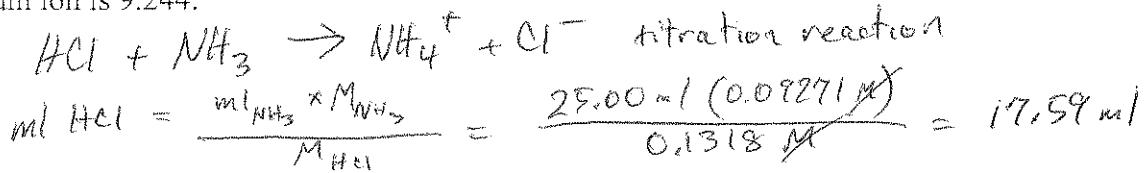
1 ml before eqpt : 16.59 ml HCl added, Most of the $NH_3$ is now $NH_4^+$, but some $NH_3$ remains : BUFFER!  $pH = 9.244 + \log \frac{1}{16.59} = 8.02$

Eqpt : Formally all $NH_3$ is Now $NH_4^+$!  Salt of weak base is a weak acid.

$$NH_4^+ + HOH \rightleftharpoons NH_3 + H_3O^+ \quad K_a = 10^{-9.244} \quad [H^+] = x \quad K_a = \frac{x^2}{F-x}$$

$$F = \frac{25 \times 0.09271}{Vol} = \frac{25 \times 0.09271}{42.6} = 0.0891\ M \quad x \cong \sqrt{K_a F} \quad pH = 5.15$$
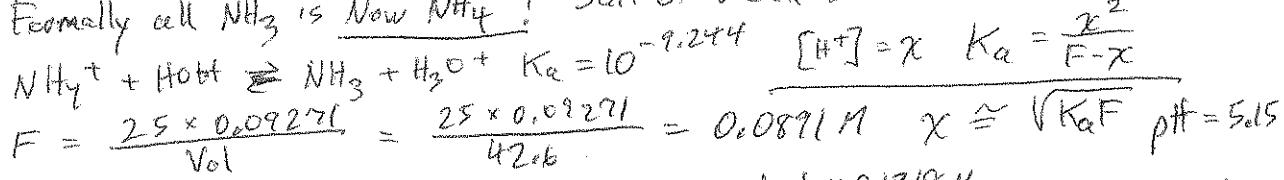
1 ml later : excess HCl determines $[H^+]$.  $[H^+] = \frac{1\ ml \times 0.1318\ M}{43.6\ ml} = 0.00302\ M$

$$pH = 2.52$$

9.	**Back titration:** A cyanide solution can be treated with **excess nickel ion** to convert the $CN^-$ to $Ni(CN)_4^{-2}$.  $Ni(CN)_4^{-2}$ is blocked from reaction with EDTA, but the **extra** $Ni^{+2}$ not complexed by cyanide can then be titrated with EDTA in order to find the original amount of cyanide.  12.73 ml of cyanide solution was mixed with 25.00 ml of 0.01709 M $Ni^{+2}$; then the back titration required 10.15 ml of 0.01307 M EDTA solution.  Write balanced reactions to explain the chemistry, and identify all Lewis acids and bases.  Find the concentration of cyanide in the original solution.

$$Ni^{+2} + 4\ CN^- \rightarrow Ni(CN)_4^{-2}$$

$$Ni^{+2} + EDTA \xrightarrow{titration} NiY^{-2}$$

total $Ni^{+2}$
$$n_{Ni^{+2}} = n_{NiY^{-2}} + n_{Ni(CN)_4^{-2}}$$

$$ml_{Ni} M_{Ni} = ml_{EDTA} M_{EDTA} + n_{Ni(CN)_4^{-2}}$$
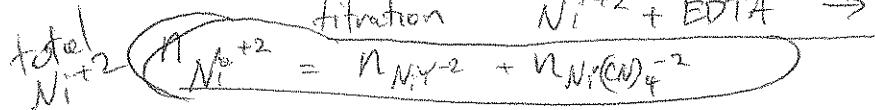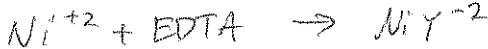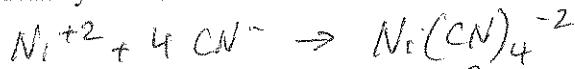
$$n_{Ni(CN)_4^{-2}} = ml_{Ni} M_{Ni} - ml_{EDTA} M_{EDTA}$$

$$\boxed{4\ n_{Ni(CN)_4^{-2}} = n_{CN^-} \text{ at the start}}$$

$$M_{CN^-} = \frac{n_{CN^-}}{Vol\ at\ the\ start}$$

$$M_{CN^-} = \frac{4\left(ml_{Ni} M_{Ni} - ml_{EDTA} M_{EDTA}\right)}{ml_{CN}}$$

$$M_{CN^-} = \frac{4\left(25(0.01709) - 10.15(0.01307)\right)}{12.73} = 0.09257\ M\ CN^-$$

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10. Sketch the titration curve for an **EDTA titration**. 30 mls of 0.010 M $ZnCl_2$ are titrated using 0.010 M EDTA. The solution is buffered to pH 9 where $\alpha_{Y-4}$ equals 0.054. The log of the formation constant of $ZnY^{-2}$ is 16.50. Compute pZn at 0, 20, 29, 30, 31, and 32 mls of EDTA added.

$$K_f' = 0.054 \quad 10^{16.50} = 1.7 \times 10^{15}$$

$$Zn^{+2} + EDTA \rightleftharpoons ZnY^{-2}$$
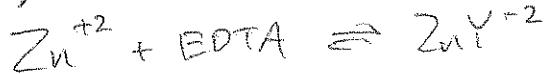
0.30 mmoles $Zn^{+2}$ at the start

| ml titr | ml tot | $[Zn^{+2}]$ | $[ZnY^{-2}]$ | excess $Y^{-2}$ | pZn |
|---------|--------|-------------|--------------|-----------------|-----|
| 0 | 30 | 0.01 | | | 2.00 |
| 20 | 50 | $\frac{0.1\text{ mmole}}{50\text{ ml}} = 2 \times 10^{-3}$ | | | 2.70 |
| 29 | 59 | $\frac{0.01}{59} = 1.7 \times 10^{-4}$ | | | 3.77 |
| 30 | 60 | | $\frac{0.3}{60} = 0.005 M$ | $1.7 \times 10^{-9}$ | 8.77 |
| 31 | 61 | | $\frac{0.3}{61}$ | $\frac{.01}{61}$ | 13.75 |
| 32 | 62 | | | | 14.05 |

$$x = [Zn^{+2}] = [Y^{-4}] \Rightarrow x = \sqrt{\frac{F-x}{K_f'}}$$

$$[Zn^{+2}] = \frac{[ZnY^{-2}]}{K_f' [EDTA]} = \frac{\frac{0.3}{61}}{1.7 \times 10^{15} \frac{0.01}{61}} = 1.76 \times 10^{-14}$$

$$\frac{\frac{0.3}{62}}{1.7 \times 10^{15} \frac{.02}{62}} = 8.8 \times 10^{-4}$$