Key to chem 103 Test 1

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Part I Multiple Choice:
1 E
2 B
3 D [H_3O^+][OH^-] = 1 \times 10^{-14} ( this is not > 1.0 \times 10^{-7})
4 A I: pH = -\log(4.2 \times 10^{-6}) = 5.4 III;pH=\log(0.25) = 0.60
5 A
6 C
7 D
8 E [H^+]=10^{-4.14}=7.24x10^{-5}; K_a=(7.24x10^{-5})2/.15=3.5x10^{-8}
9 B pKa should be closest to 4.20.
   pKa = -logKa: These are respectively: 4.74, 4.20, 3.74, 3.14, 3.35
10 D
11 C
12 B
13 D MV = M'V' V = M'V'/M = (50.00 \text{mL})(.0950)/(.1060) = 44.81 \text{mL}
15 B AgCl <=> Ag+ + Cl x(.154M) = 1.8x \cdot 10^{-10} x = (1.8x \cdot 10^{-10})/(.154M) = 1.2x \cdot 10^{-9}
16 B
17 C pH = 14-pOH = 14.00 - (-\log 1.0 \times 10^{-4}) = 10.0
18 E [H^+] = 1.0M(1.0mL/(100)mL = 0.01 M HCl; pH = -\log(.01)=2.0
19 B HOAc <=> H+ + OAc- x^2/0.10 \approx 1.8 \times 10^{-5}; x = 1.34 \times 10^{-3} pH =-logx=2.9
20 B Ca<sup>2+</sup> + EDTA <==> CaEDTA 1.0/x^2 \approx 4.5 \times 10^{10} => x^2 = 2.2 \times 10^{-11} x = 4.7 \times 10^{-6}
                                 1.0-x
Part II
21
     HA + H_2O \rightleftharpoons A^- + H_3O^+
     A^{-} + H_2O \rightleftharpoons HA + OH^{-}
b.
    Now K_{a,HA} = \frac{[A^-][H_3O^+]}{[HA]} and K_{b,A^-} = \frac{[HA][OH^-]}{[A^-]}. Thus,
    K_{a,HA} \times K_{b,A^{-}} = \frac{[A^{-}][H_{3}O^{+}]}{[HA]} \times \frac{[HA][OH^{-}]}{[A^{-}]} = [H_{3}O^{+}][OH^{-}] = K_{w} = 1.0 \times 10^{-14}.
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22 The declining pH (i.e., declining [OH-]) clearly indicates that something is reacting with the OH $^-$ ions. Carbonate, already in the fully deprotonated form, cannot react with CO_3^{2-} , but Cu^{2+} can, to form $Cu(OH)_2(s)$. Thus, it seems likely that a small amount of $CuCO_3$ is continually dissolving, but that the free Cu^{2+} ions in solution then react with OH $^-$ ions to precipitate $Cu(OH)_2$. The precipitate changes appearance because it is, at least to some extent, a different precipitate.

The net reaction is $CuCO_3 + 2 OH_3 = Cu(OH)_2 + CO_3^2$. The K_{rxn} for this is easily

shown to be =
$$\frac{K_{sp}(CuCO_3)}{K_{sp}(Cu(OH)_2)} = \frac{2.5 \times 10^{-10}}{1.6 \times 10^{-19}} = 1.6 \times 10^9$$
. Thus, the reaction is heavily

product-favored. The student was in fact successful; the CuCO₃ does dissolve, and to a greater extent than it would in water. However, the Cu²⁺ ions immediately re-precipitate.

23

- a. The equivalence point of an acid-base titration is the point at which the number of moles of acid is exactly equal to the number of moles of base. The endpoint of a titration is the point at which we *think* the equivalence point has been reached in this case, when the indicator changes.
- b. The pH rises fairly rapidly near the equivalence point. If the indicator is indicating the end of the titration prematurely, then it must be changing colour at too low a pH. Another indicator should be selected, one with its color transition range centered as closely as possible on the predicted pH at the equivalence point.

24. solution:

- a) $V_2 = 12.5$ is half equiv. so: pH =pKa + log[base]/[acid] = 3+log1 = 3.0
- b) $V_2 = 37.5$, 1.5 equivalence so, pH= pKa2 +0 = 6.0
- c) isoionic point: (1/2)(6+10) = 8

B.
$$pI = 3+6/2 = 4.5$$

25

For PbI₂, $K_{sp} = [Pb2+][I-]^2 => [I^-] = \sqrt{(K_{sp}/[Pb^{2+}])}$. When PbI₂ first starts to precipitate, $[Pb^{2+}] = 0.100 \text{ M}$

=>
$$[I^{-}] = \sqrt{(K_{sp}/[Pb^{2+}])} = \sqrt{((8.7 \times 10^{-9})/0.100)} = 2.9 \times 10^{-4} \text{ M}.$$

For TII, $K_{sp} = [Tl^+][I^-] => [Tl^+] = K_{sp}/[I^-]$. Thus, at the point when PbI₂ first starts to precipitate

$$[T1^+] = K_{sp}/[I^-] = (6.0 \times 10^{-8})/(2.9 \times 10^{-4}) = 2x10^{-4}$$

Since we we have 1.0 x 10⁻³ M Tl to start with,

this means % remaining Tl is $(2x10^{-4})(100\%)/(1.0 \times 10^{-3})=20\%$ remains, 80% recovered.