Exam 1
Analytical 1
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1)

0.97 g of sodium hypochlorite (NaOCl, FW 74.442 g/mol) was transferred to a 100.00 ml volumetric flask, diluted to the mark with de-ionized water, and thoroughly mixed. Calculate the pH of this solution. (20 pts)

$NaOCl(aq) \rightarrow Na^+ + OCl^-$

OCl- is the conjugate base of HOCl
$Ka(HOCl) = 3.0*10^{-7}$ (from App. G, AP 20)

$[OCl-] = (0.97\ g\ NaOCl)(1mol/74.442\ g)*(1/0.10000\ L) = 0.13028\ M$
(4 pts)
Since OCl^- is a weak base, it associates with water

$OCl^- + H_2O \leftrightarrow HOCl + OH^-$ (4 pts)

The equilibrium constant is Kb

$Kb = Kw/Ka = 1.00*10^{-14}/3.0*10^{-8} = 3.33*10^{-7}$ (4 pts)

$Kb = [OH^-]^2/ F_{OCl-}$

$[OH-] =(3.33*10^{-7}*0.1308)^{1/2} = 2.084*10^{-4}\ M$ (4 pts)

$[H^+] = Kw/[OH-] = 1.00*10^{-14}/2.084*10^{-4} = 4.698*10^{-11}$

$pH = -log[H^+] = 10.3189$

There really is only 2 significant figures in [H+] because there are only two sig figs in the initial weight 0.97 g. So…..

pH = 10.32 (4 pts)

2)

If 25.00 ml of the solution in problem 1 is titrated with an HCl solution, and it takes 32.18 ml of the dilute HCl (strong acid) solution to reach the endpoint of the titration (assume an ideal indicator was used), calculate the pH of the solution at the endpoint of the titration. (20 pts)

At the equivalence point the OCl^- has been completely converted to HOCl.
(4 pts)
F_{HOCl} = (25.00 ml)*(0.130303 M)/(25.00+32.18 ml) = 0.05697 M
(4 pts)
The relevant equilibrium is dissociation of HOCl in water

$HOCl + H_2O \leftrightarrow OCl^- + H_3O^+$ (4 pts)

The equilibrium constant is Ka

$Ka = 3.0*10^{-8} = [H_3O^+]^2 / F_{HOCl}$

$[H_3O^+] = (3.0*10^{-8}*0.05697)^{1/2} = 4.1341*10^{-5}$ M (4 pts)

$pH = -\log[H_3O^+] = 4.38362$

There really is only 2 significant figures in [H+] because there are only two sig figs in the initial weight 0.97 g. So…..

pH = 4.38 (4 pts)

3) **Calculate the pH a 0.11 M histidine solution. (15 pts)**

From App. G, AP19 ⇒ Histidine is a triprotic acid (3 pts) and its most acidic species has the form H_3B^{2+}. So the four forms are….
(3 pts)
H_3B^{2+}
H_2B^+
HB
B^-

The Kas are (3 pts)
$K_{a1} = 2*10^{-2}$
$K_{a2} = 9.5*10^{-7}$
$K_{a3} = 8.3*10^{-10}$
F = 0.11 M

The neutral species is HB and it is the second intermediate species. Therefore,

$[H^+] = [(K_2K_3F+KwK_1)/(K_1+F)]^{1/2}$

if you check the math for these Ka values, you will find that this reduces to…

$= (K_2K_3)^{1/2} = 2.808*10^{-8}$ M (3 pts)

$pH = -\log[H^+] = 7.55$, $[H^+]$ really only has two sig figs.
(3 pts)

4)

1L of fresh 0.05 M phosphate buffer is prepared by adding 4.25 g of very pure anhydrous KH_2PO_4 (FW 136.086 g/mol) and 2.67 g of very pure anhydrous Na_2HPO_4 (FW 141.959 g/mol) to a 1.000 L flask and diluting to the mark with de-ionized water. Calculate the pH of this buffer solution. (12 pts)

When you dissolve these two salts in water, you get…

$KH_2PO_4 \rightarrow K^+ + H_2PO_4^-$
$Na_2HPO_4 \rightarrow 2Na^+ + HPO_4^{2-}$

$H_2PO_4^-$ and HPO_4^{2-} are the two intermediate species in the phosphoric acid system and they are an acid-base conjugate pair. Mixture of a conjugate pair is a buffer, and Henderson-Hasselbalch applies

$pH = pKa2 + \log(\text{moles } HPO_4^{2-}/\text{mol } H_2PO_4^-)$ 3 pts

moles HPO_4^{2-} = (2.67 g)*(1 mol/141.959 g) = 0.018808 moles 3 pts
mol $H_2PO_4^-$ = (4.25 g)*(1mol/136.086 g) = 0.031230 moles 3 pts

pH = 7.199 + log (0.018808/0.031230) = 6.979 3 pts

The mole calculation gives three sig figs, and when we take the log of the ratio we get three sig figures after the decimal place.

5)

A 0.521 M trans-butenedioic acid solution is buffered to a pH of 4.23. Using alpha fractions, calculate the concentration of the HB^- species in this solution. Is HB^- the principle species? 15 pts

Trans-butenedioic acid is a diprotic acid 3 pts
From App G, AP 17
$K_{a1} = 8.84*10^{-4}$
$K_{a2} = 3.21*10^{-5}$

$[H^+] = 10^{-pH} = 10^{-4.23} = 5.888*10^{-5}$ M (3 pts)

$[HB^-]/F = \alpha_{HB-} = K_1[H^+]/\{[H^+]^2 + K_1[H^+] + K_1K_2\}$ 3 pts

$[H^+]^2 = 3.4669*10^{-9}$
$K_1[H^+] = 5.2050*10^{-8}$
$K_1K_2 = 2.8376*10^{-8}$
$[H^+]^2 + K_1[H^+] + K_1K_2 = 8.38923*10^{-8}$

$\alpha_{HB-} = 5.2050*10^{-8}/8.38923*10^{-8} = 0.6204$

$[HB^-] = F* \alpha_{HB-} = 0.512*0.6204 = 0.323$ M 3 pts

62 % of the t-butenedioic acid is in the BH^- form, so it has to be the principle species. 3 pts

6)

Using activities calculate the Ag^+ concentration in a solution that is saturated with Ag_2CrO_4 and contains 0.03333 M of K_2CrO_4. What percentage of the CrO_4^{2-} in solution is derived from the Ag_2CrO_4? 18 pts

$Ksp(Ag_2CrO_4) = [Ag^+]^2\gamma^2_{Ag}\,[CrO_4^{2-}]\gamma_{CrO4}$ 3 pts

K_2CrO_4 dissociates in water to give K^+ and CrO_4^{2-}.
$K_2CrO_{4(aq)} \rightarrow 2K^+ + CrO_4^{2-}$
The other source of CrO_4^{2-} is from the relatively insoluble salt Ag_2CrO_4. So this is a common ion problem.

$Ksp(Ag_2CrO_4) = 1.2*10^{-12}$ (from App F, AP12) $= [Ag^+]^2[CrO_4^{2-}]$
Ksp is small and it is reasonable to expect that the vast majority of CrO_4^{2-} is coming from K_2CrO_4.
Therefore, 3 pts
$[CrO_4^{2-}] = 0.03333$ M
$[K^+] = 0.06667$ M
$[Ag^+]$ = small

$\mu = ½\{[CrO_4^{2-}]\,(-2)^2 + [K^+]\,(+1)^2\} = 0.10$ M 3 pts
from Table 8-1 3 pts
$\gamma_{Ag} = 0.75$
$\gamma_{CrO4} = 0.355$

$Ksp(Ag_2CrO_4) = [Ag^+]^2\gamma^2_{Ag}\,[CrO_4^{2-}]\gamma_{CrO4}$
$1.2*10^{-12} = [Ag^+]^2(0.75)^2_{Ag}\,[0.03333](0.355)$

$[Ag^+] = 1.3*10^{-5}$ M (2 sig figs in the activity coefficient)
$[CrO_4^{2-}]$from $Ag_2CrO_4 = [Ag^+]/2 = 6.7*10^{-6}$ M 3 pts

% derived from $Ag_2CrO_4 = \{(6.7*10^{-6})/(0.0333367)\}*100 = 0.020$ %
3 pts