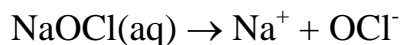


Exam 1
Analytical 1
Evans
Fall 2001

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)



OCl⁻ is the conjugate base of HOCl

$$K_a(\text{HOCl}) = 3.0 \times 10^{-7} \quad (\text{from App. G, AP 20})$$

$$[\text{OCl}^-] = (0.97 \text{ g NaOCl})(1 \text{ mol}/74.442 \text{ g}) \cdot (1/0.10000 \text{ L}) = 0.13028 \text{ M}$$

(4 pts)

Since OCl⁻ is a weak base, it associates with water



The equilibrium constant is K_b

$$K_b = K_w/K_a = 1.00 \times 10^{-14}/3.0 \times 10^{-7} = 3.33 \times 10^{-7} \quad (4 \text{ pts})$$

$$K_b = [\text{OH}^-]^2 / F_{\text{OCl}^-}$$

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

$$[\text{H}^+] = K_w/[\text{OH}^-] = 1.00 \times 10^{-14}/2.084 \times 10^{-4} = 4.698 \times 10^{-11}$$

$$\text{pH} = -\log[\text{H}^+] = 10.3189$$

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

$$\text{pH} = 10.32 \quad (4 \text{ pts})$$

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)

$$F_{\text{HOCl}} = (25.00 \text{ ml}) \cdot (0.130303 \text{ M}) / (25.00 + 32.18 \text{ ml}) = 0.05697 \text{ M}$$

(4 pts)

The relevant equilibrium is dissociation of HOCl in water



The equilibrium constant is K_a

$$K_a = 3.0 \cdot 10^{-8} = [\text{H}_3\text{O}^+]^2 / F_{\text{HOCl}}$$

$$[\text{H}_3\text{O}^+] = (3.0 \cdot 10^{-8} \cdot 0.05697)^{1/2} = 4.1341 \cdot 10^{-5} \text{ M} \quad (4 \text{ pts})$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 4.38362$$

There really is only 2 significant figures in $[\text{H}^+]$ because there are only two sig figs in the initial weight 0.97 g. So.....

$$\text{pH} = 4.38 \quad (4 \text{ pts})$$

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

From App. G, AP19 \Rightarrow 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)



The Kas are (3 pts)

$$K_{a1} = 2 \cdot 10^{-2}$$

$$K_{a2} = 9.5 \cdot 10^{-7}$$

$$K_{a3} = 8.3 \cdot 10^{-10}$$

$$F = 0.11 \text{ M}$$

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

$$[H^+] = [(K_2K_3F + K_wK_1)/(K_1 + F)]^{1/2}$$

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

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

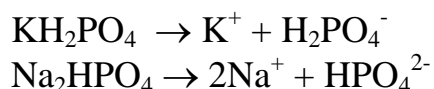
$$\text{pH} = -\log[H^+] = 7.55, [H^+] \text{ really only has two sig figs.}$$

(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...



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

$$\text{pH} = \text{pKa}_2 + \log (\text{moles } \text{HPO}_4^{2-} / \text{mol } \text{H}_2\text{PO}_4^-) \quad 3 \text{ pts}$$

$$\text{moles } \text{HPO}_4^{2-} = (2.67 \text{ g}) * (1 \text{ mol} / 141.959 \text{ g}) = 0.018808 \text{ moles} \quad 3 \text{ pts}$$

$$\text{mol } \text{H}_2\text{PO}_4^- = (4.25 \text{ g}) * (1 \text{ mol} / 136.086 \text{ g}) = 0.031230 \text{ moles} \quad 3 \text{ pts}$$

$$\text{pH} = 7.199 + \log (0.018808 / 0.031230) = 6.979 \quad 3 \text{ pts}$$

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

$$K_{a1} = 8.84 \times 10^{-4}$$

$$K_{a2} = 3.21 \times 10^{-5}$$

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

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

$$[\text{H}^+]^2 = 3.4669 \times 10^{-9}$$

$$K_1[\text{H}^+] = 5.2050 \times 10^{-8}$$

$$K_1K_2 = 2.8376 \times 10^{-8}$$

$$[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2 = 8.38923 \times 10^{-8}$$

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

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

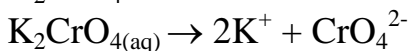
62 % of the t-butenedioic acid is in the BH^- form, so it has to be the principle species. **3 pts**

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**

$$K_{\text{sp}}(\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+]^2 \gamma_{\text{Ag}}^2 [\text{CrO}_4^{2-}] \gamma_{\text{CrO}_4} \quad \mathbf{3 \text{ pts}}$$

K_2CrO_4 dissociates in water to give K^+ and 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.

$$K_{\text{sp}}(\text{Ag}_2\text{CrO}_4) = 1.2 \times 10^{-12} \text{ (from App F, AP12)} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

K_{sp} 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**

$$[\text{CrO}_4^{2-}] = 0.03333 \text{ M}$$

$$[\text{K}^+] = 0.06667 \text{ M}$$

$$[\text{Ag}^+] = \text{small}$$

$$\mu = \frac{1}{2} \{ [\text{CrO}_4^{2-}] (-2)^2 + [\text{K}^+] (+1)^2 \} = 0.10 \text{ M} \quad \mathbf{3 \text{ pts}}$$

from Table 8-1 **3 pts**

$$\gamma_{\text{Ag}} = 0.75$$

$$\gamma_{\text{CrO}_4} = 0.355$$

$$\begin{aligned} K_{\text{sp}}(\text{Ag}_2\text{CrO}_4) &= [\text{Ag}^+]^2 \gamma_{\text{Ag}}^2 [\text{CrO}_4^{2-}] \gamma_{\text{CrO}_4} \\ 1.2 \times 10^{-12} &= [\text{Ag}^+]^2 (0.75)^2_{\text{Ag}} [0.03333] (0.355) \end{aligned}$$

$$[\text{Ag}^+] = 1.3 \times 10^{-5} \text{ M (2 sig figs in the activity coefficient)}$$

$$[\text{CrO}_4^{2-}]_{\text{from Ag}_2\text{CrO}_4} = [\text{Ag}^+]/2 = 6.7 \times 10^{-6} \text{ M} \quad \mathbf{3 \text{ pts}}$$

$$\% \text{ derived from Ag}_2\text{CrO}_4 = \{ (6.7 \times 10^{-6}) / (0.0333367) \} * 100 = 0.020 \%$$

3 pts

