

Review Sheet #2, Wednesday December 10, 2003

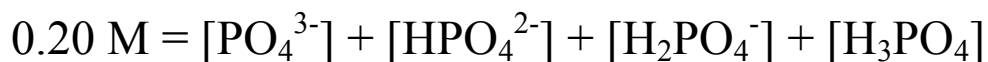
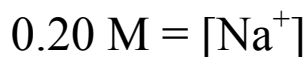
1] Write the MBE for 0.050 F CH₃COOH (aq). (1 minute)



2] Write the CBE for 0.050 F CH₃COOH (aq). (1 minute)



3] Write the MBE & CBE for 0.20 M NaH₂PO₄(aq). (2 minutes)



4] Write the MBE and CBE for PbI_2 dissolved into water. Note that PbI^+ , $\text{PbI}_2(\text{aq})$, PbI_3^- , PbOH^+ , H_2O , H^+ , & OH^- are formed from the dissolution of PbI_2 . (5 minutes)

MBE

Begin with $2[\text{Pb}^{2+}] = [\text{I}^-]$ then realize that:

$$2\{[\text{Pb}^{2+}] + [\text{PbI}^+] + [\text{PbI}_2(\text{aq})] + [\text{PbI}_3^-] + [\text{PbOH}^+]\} =$$

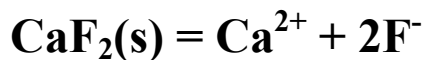
$$[\text{I}^-] + [\text{PbI}^+] + 2[\text{PbI}_2] + 3[\text{PbI}_3^-]$$

CBE

$$[\text{H}^+] + [\text{PbI}^+] + [\text{PbOH}^+] + 2[\text{Pb}^{2+}]$$

$$= [\text{I}^-] + [\text{PbI}_3^-] + [\text{OH}^-]$$

5] Calculate the solubility of CaF_2 , $K_{\text{sp}} = 3.9\text{e-}11$, at pH 3.00 (10 minutes)



5] Answer

CBE is not possible since we cannot know the charge situation arising from the buffer.

$$\text{MBE} \quad 2[\text{Ca}^{2+}] = [\text{F}^-] + [\text{HF}]$$

$$\text{Other eqn:} \quad K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2 = 3.9\text{e-}11$$

$$K_{\text{b}} = [\text{HF}][\text{OH}^-] / [\text{F}^-] = 1.5\text{e-}11$$

$$K_{\text{w}} = [\text{H}^+][\text{OH}^-] = 1.0\text{e-}14$$

$$\text{@ pH 3.00} \quad [\text{OH}^-] = 1.0\text{e-}11$$

$$\begin{aligned} \text{Therefore} \quad & [\text{HF}] / [\text{F}^-] = 1.5\text{e-}11 / 1.0\text{e-}11 = 1.5 \\ & [\text{HF}] = 1.5 * [\text{F}^-] \end{aligned}$$

$$\text{Plug back into MBE:} \quad 2[\text{Ca}^{2+}] = [\text{F}^-] + 1.5[\text{F}^-] = 2.5[\text{F}^-]$$

$$0.8[\text{Ca}^{2+}] = [\text{F}^-]$$

$$\text{Plug into } K_{\text{sp}}: \quad [\text{Ca}^{2+}]0.8[\text{Ca}^{2+}]^2 = 3.9\text{e-}11$$

$$[\text{Ca}^{2+}] = 3.9\text{e-}4 \text{ M}$$

6] Calculate the pH of a 1.0e-3 M solution of NaHCO₃,

$$K_{a1} = 4.5e-7$$

$$K_{a2} = 5.6e-11 \quad (2 \text{ min})$$

$$\text{pH} = \frac{1}{2} (\text{p}K_1 + \text{p}K_2) = \frac{1}{2}(6.35 + 10.25) = 8.30$$

A more rigorous solution gives 8.26

In general for H_nA

$$D = [\text{H}^+]^n + K_{a1}[\text{H}^+]^{n-1} + K_{a1}K_{a2}[\text{H}^+]^{n-2} + \dots + K_{a1}K_{a2}K_{a3}\dots K_{an}$$

$$\alpha_{\text{H}_n\text{A}} = [\text{H}^+]^n/D$$

$$\alpha_{\text{H}_{n-1}\text{A}} = K_{a1}[\text{H}^+]^{n-1}/D$$

$$\alpha_{\text{H}_{n-j}\text{A}} = K_{a1} K_{a2}\dots K_j[\text{H}^+]^{n-j}/D$$

7] What is the fraction of NH₄⁺ in the HA and A forms at pH 10.38? K_a = 5.70e-10 (2.5 minutes)

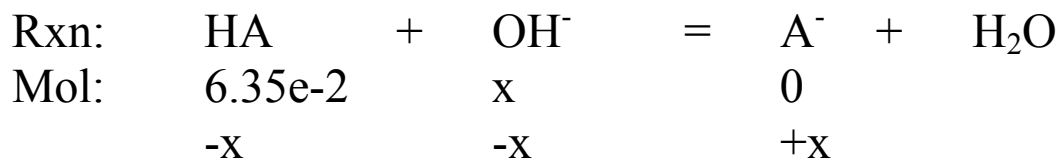
$$D = [\text{H}^+]^1 + K_{a1}[\text{H}^+]^0 = 4.17\text{e-}11 + 5.70\text{e-}10 = 6.12\text{e-}10$$

$$\alpha_{\text{HA}} = 4.17\text{e-}11 / 6.12\text{e-}10 = 0.068$$

$$\alpha_{\text{A}} = 5.70\text{e-}10 / 6.12\text{e-}10 = 0.93$$

8] How many mL of 0.500 M NaOH should be added to 10.0 g of HA (157.597 g/mol) to give a pH 7.60 in a final volume of 250 mL? $K_a = 8.41\text{e-}9$ (7 minutes).

$$\text{Mol HA} = 10.0 \text{ g} * (\text{mol} / 157.597 \text{ g}) = 6.35\text{e-}2$$



$$[\text{HA}] = (6.35\text{e-}2 - x) \quad \& \quad [\text{OH}^-] = [\text{A}^-] = x$$

$$[\text{H}^+] = 2.51\text{e-}8 \text{ M}$$

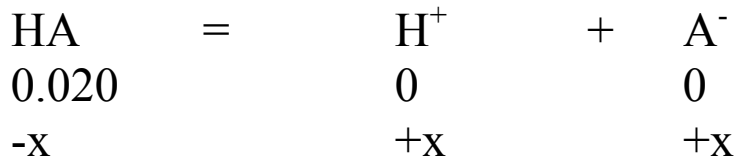
$$K_a = [\text{H}^+][\text{A}^-] / [\text{HA}] \quad 8.41\text{e-}9 = 2.51\text{e-}8 x / (6.35\text{e-}2 - x)$$

$$x = 1.59\text{e-}2 \text{ mol}$$

$$1.59\text{e-}2 \text{ mol} * (\text{L} / 0.500 \text{ mol}) = 31.9 \text{ mL}$$

Titration of weak acid with strong base.

9] Calculate pH of 50.00 mL of 0.0200 M HA with pKa = 6.15 before any base is added. (2 minutes)



$$x^2 / 0.0200 - x = 7.08e-7$$

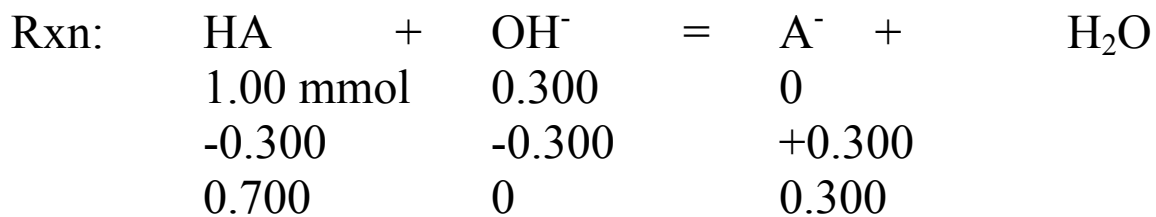
$$x = 1.19e-4$$

$$[H^+] = 3.92$$

10] pH when 3.00 mL of 0.100 M NaOH is added. (5 minutes)

Initial HA = 50.00 * 0.0200 = 1.00 mmol

OH⁻ added = 0.300 mmol



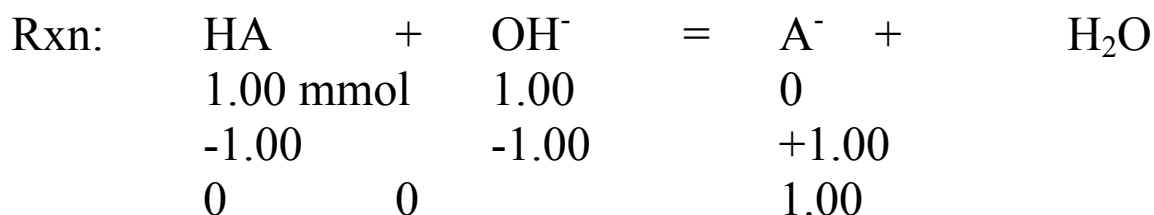
Buffer system $K_a = [H^+][A^-] / [HA]$

$$[H^+] = K_a [HA] / [A^-] = 7.08e-7 * 0.700 / 0.300$$

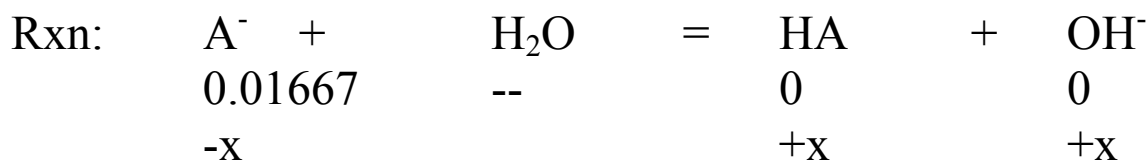
$$pH = 5.78$$

11] pH when 10.00 mL of 0.100 M NaOH is added (5 minutes).

OH⁻ added = 1.00 mmol we are at the eq. pt.



$$[A^-] = 1.00 \text{ mmol} / 60.00 \text{ mL} = 0.01667 \text{ M}$$



$$K_b = K_w / K_a = 1.41e-8 = x^2 / (0.01667 - x)$$

$$x = 1.533e-5$$

$$\text{pH} = 9.19$$

12] pH when 10.10 mL of 0.100 M NaOH is added (2 minutes).

$$\text{Excess OH}^- = 0.10 \text{ mL} * 0.100 \text{ M} = 0.010 \text{ mmol}$$

$$[\text{OH}^-] = 0.010 \text{ mmol} / 60.10 \text{ mL} = 1.66\text{e-}4 \text{ M}$$

$$\text{pH} = 10.22$$

