

Chem 103 – lecture 3b

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Today:

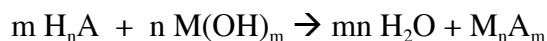
0. Review: equivalence point calculations
- 1 Henderson-Hasselbalch Equation.
2. pH calculations in titrations using HH equation
3. calculating pH for polyprotic acids/bases.

Lecture:

(0) review titration:

at equiv pt: # equiv H^+ donated = #equiv H^+ accepted#eq H^+ donated = $n \times$ moles H_nA ;# H^+ accepted = $m \times$ moles $M(OH)_m$ so if the titration is between H_nA and $M(OH)_m$ @ eq pt : $n \times$ moles $H_nA = m \times$ moles $M(OH)_m$ but moles of solute = $\frac{\text{mol solute}}{\text{solution}} \times L$ solutionso, $n M_1 V_1 = m M_2 V_2$ where 1 = H_nA and 2 = $M(OH)_m$ so $M_1 = (m/n)(M_2 V_2 / V_1)$

another way to solve it:

write titration reaction: use: 1 = H_nA and 2 = $M(OH)_m$ Say titrate V_1 of the acid, requiring V_e of M^o_2 of the base.

$$\text{Then } M_1 = \frac{M_2 V_e (m \text{ mol } H_nA)}{V_1 \quad n \text{ mol } M(OH)_m}$$

The **Henderson Hasselbalch** equation:

$$K_a = \frac{[H^+][A^-]}{[HA]} ; \text{ take the } -\log \text{ of both sides and}$$

rearrange:

$$-\log K_a = -\log[H^+] - \log \frac{[A^-]}{[HA]} \text{ or,}$$

$$-\log[H^+] = -\log K_a + \log \frac{[A^-]}{[HA]}, \text{ or}$$

$$\text{pH} = \text{pK}_a + \log \frac{[A^-]}{[HA]}$$

base ←

← *acid*

Let's try it:

Example: To a buffer solution of volume V_o containing M_A A^- and M_b A^- is added V_{HX} volume of M_{HZ} strong acid HX. HA has a given pK_a . What is the resulting pH?

OK:

$$\text{pH} = \text{pK}_a + \log \frac{[A^-]}{[HA]} = \text{pK}_a + \log \frac{(M_{A^-} V_o - M_{HX} V_{HX}) / V_{\text{total}}}{(M_{HA} V_o + M_{HX} V_{HX}) / V_{\text{total}}}$$

moles A^- initially moles HX added $(V_o + V_{HX})$
 moles HA initially moles HX added $(V_o + V_{HX})$

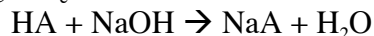
Try using the HH equation for the titration of acetic acid with NaOH.

Example: Using the buffer equation, determine the pH during the titration of 25.0 mL of 0.100 M acetic acid with 0.100 M NaOH, at the following V_{NaOH} 's:

- a) $V_{\text{NaOH}} = 10.0$ mL, b) $V_{\text{NaOH}} = 12.5$ mL,
 c) $V_{\text{NaOH}} = 17.0$ mL. ($\text{pK}_a = 4.75$ for acetic acid, HA)

Solution:

First, get V_e : 1-to-1 titration since the equation is:



So, it's $M_{\text{HA}} V_{\text{HA}} = M_{\text{NaOH}} V_e$; or: $V_e = \frac{M_{\text{HA}} V_{\text{HA}}}{M_{\text{NaOH}}}$

$$V_e = \frac{(0.100\text{M})(25.0\text{mL})}{(0.100\text{M})} = 25.0 \text{ mL}$$

$$\text{pH} = \text{pK}_a + \log \frac{n_{\text{A}^-}/V_{\text{total}}}{n_{\text{HA}}/V_{\text{total}}} = \text{pK}_a + \log \frac{n_{\text{A}^-}}{n_{\text{HA}}} = \text{pK}_a + \log \frac{n_{\text{NaOH}}}{n_{\text{HA}}^0 - n_{\text{NaOH}}}$$

$$\text{pH} = \text{pK}_a + \log \frac{M_{\text{NaOH}}^0 V_{\text{NaOH}}}{M_{\text{HA}}^0 V_{\text{HA}}^0 - M_{\text{NaOH}}^0 V_{\text{NaOH}}} \quad \text{but} \quad M_{\text{HA}}^0 V_{\text{HA}}^0 = M_{\text{NaOH}}^0 V_e$$

$$\text{and so: } \text{pH} = \text{pK}_a + \log \frac{M_{\text{NaOH}}^0 V_{\text{NaOH}}}{M_{\text{NaOH}}^0 V_e - M_{\text{NaOH}}^0 V_{\text{NaOH}}}$$

$$\text{and : } \text{pH} = \text{pK}_a + \log \frac{M_{\text{NaOH}}^0 V_{\text{NaOH}}}{M_{\text{NaOH}}^0 (V_e - V_{\text{NaOH}})} = \text{pK}_a + \log \frac{V_{\text{NaOH}}}{V_e - V_{\text{NaOH}}}$$

so let's apply it:

$$\text{a) } V_{\text{NaOH}} = 10.0\text{mL: } \text{pH} = 4.75 + \log \frac{10.0}{25.0 - 10.0}$$

b)