Homework 02 Solutions

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Course: 03-232 A
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Task 1

(a) See Figure (a)

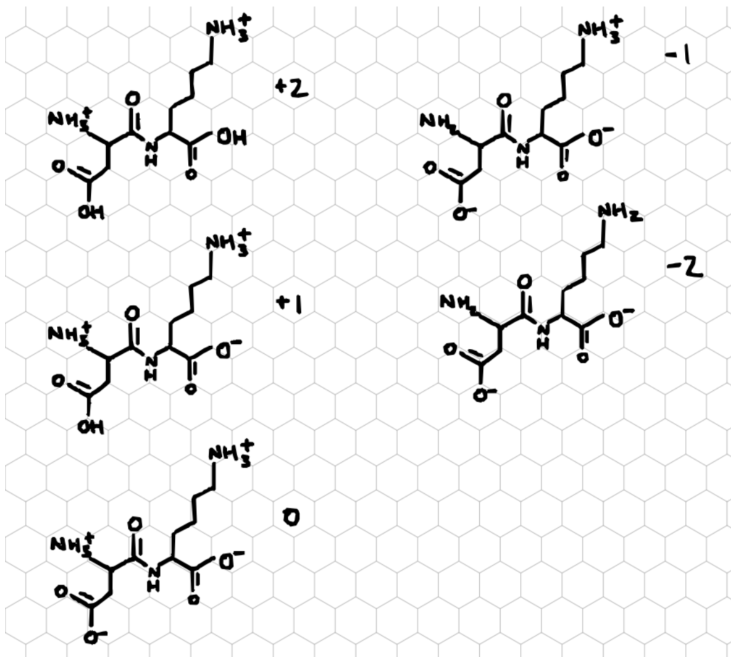

Figure 1: Asp-Lys species across protonation states

(b) See Figure (b)

(c) C terminus: pH $= 4 >$ p$K_a = 2$, so net charge is -1
Asp side chain: pH $= 4 =$ p$K_a = 4$, so net charge is -0.5
N terminus chain: pH $= 4 <$ p$K_a = 9$, so net charge is $+1$
Lys side chain: pH $= 4 <$ p$K_a = 11$, so net charge is $+1$
avg. net charge: (+1) + (+1) + (-1) + (-0.5) = $\boxed{0.5}$

(d) C terminus: pH $= 7 >$ p$K_a = 2$, so net charge is -1
Asp side chain: pH $= 7 >$ p$K_a = 4$, so net charge is -1
N terminus chain: pH $= 7 <$ p$K_a = 9$, so net charge is $+1$
Lys side chain: pH $= 7 <$ p$K_a = 11$, so net charge is $+1$
avg. net charge: (+1) + (+1) + (-1) + (-1) = $\boxed{0}$

(e) C terminus: pH $= 9 <$ p$K_a = 2$, so net charge is -1
Asp side chain: pH $= 9 <$ p$K_a = 4$, so net charge is -1

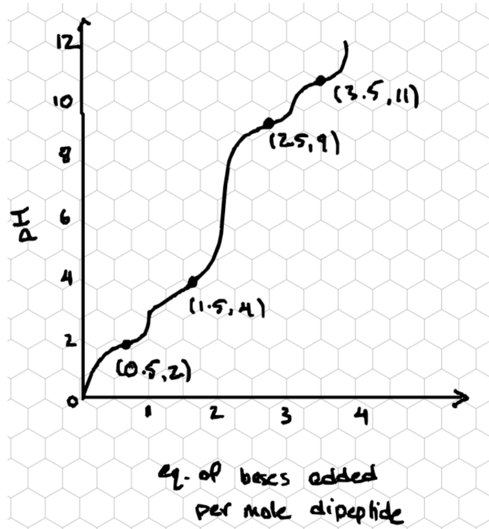

Figure 2: Titration curve for Asp-Lys

N terminus chain: pH $= 9 =$ p$K_a = 9$, so net charge is $+0.5$
Lys side chain: pH $= 9 >$ p$K_a = 11$, so net charge is $+1$
avg. net charge: (-1) + (-0.5) + (+1) + (+1) = $\boxed{-0.5}$

(f) The net 0 species occurs between pK_a that bracket the neutral form:

$$\mathrm{p}I \approx (4+9)/2 = \boxed{6.5}$$

Task 2

(a) $0.02\ \mathrm{mol/L} \cdot 0.500\ \mathrm{L} = \boxed{0.010\ \mathrm{mol}}$

(b) Use the base, since HEPES starts in the most acidic form $\mathrm{H_2A}$.

(c) At $\mathrm{pH} = 7.1$, the equilibrium that is relevant is the second dissocation between $\mathrm{HA^-}$ and $\mathrm{A^{2-}}$. Using Henderson-Hasselbalch,

$$\frac{[\mathrm{A^{2-}}]}{[\mathrm{HA^-}]} = 10^{7.1-7.5} \approx 0.398.$$

Because there are a total of 0.010 moles, so the number of moles of $\mathrm{A^{2-}}$ is 0.00285 and the number of moles of $\mathrm{HA^-}$ is 0.00715. It takes two moles of $\mathrm{OH^-}$ to make the former, and one mole for the latter. Then, we can take a weighted average:

$$\text{moles of OH}^- = 1 \cdot 0.00715 + 2 \cdot 0.00285 = 0.01285\ \text{mol}.$$

Because [KOH] $= 1\mathrm{M}$, this is equivalent to $\boxed{12.85\ \mathrm{mL}}$ of KOH.

Task 3

(a) At $\mathrm{pH} = 7.1$, the buffer has 7.15 mmol of $\mathrm{HA^-}$ and 2.85 mmol of $\mathrm{A^{2-}}$. Adding base converts the protonated form to the unprotonated form, so there will be 7.10 mmol and 2.90 mmol of each, respectively. Appyling Henderson-Hasselbalch gives

$$\mathrm{pH} = 7.5 + \log(2.90/7.10) \approx \boxed{7.11}$$

(b) The pH only changed by 0.01, a relatively insignificant change.

(c) The KOH dissocatiates completely, so $[\mathrm{OH}^-] = 5 \cdot 10^5 \text{ mol}/0.50 \text{ L} = 10 \cdot 10^-4 \text{ M}$. Taking the negative log gives a pH of $\boxed{10.00}$.

Task 4

(a) We have

$$\varepsilon_{\textsf{protein}} = 3\varepsilon(\textsf{Trp}) + 3\varepsilon(\textsf{Tyr}) = 15150 + 4470 = 19620 \text{ M}^{-1}\text{cm}^{-1}.$$

Then,

$$c = \frac{A}{\epsilon \ell} = \boxed{5.61 \cdot 10^{-5} \text{ M}}.$$

(b) There are $cV = (5.61 \cdot 10^-5)(1.0 \cdot 10^-3) = 5.61 \cdot 10^{-8}$ moles of the protein. Then, the mass is $(5.61 \cdot 10^-8)(20000) = \boxed{1.12 \cdot 10^-3 \text{ g}}$.